Text-Books of Physical Chemistry

EDITED BY

SIR WILLIAM RAMSAY K.C.B., F.R.S.

AND

F. G. DONNAN, C.B.E., M.A., Ph.D., F.I.C., F.R.S.

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SPECTROSCOPY

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SPECTROSCOPY

BY

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PREFACE TO VOLUME III.

In accordance with the scheme outlined in the preface to the second volume there are discussed in this volume those developments in spectroscopy which are the more immediate results of the Bohr theory. Whilst such discussion necessarily involves the description of much experimental work, the principal advances in atomic theory, so far as they fall within the purview of spectral radiation, find a place here. In committing this volume to the press, I confess to a humbleness of mind born of the difficulty of adequately recording the remarkable progress of the last fourteen years. To speak in terms of analogy the subject is so large that a principle of selection must of necessity be exercised, and in a real endeavour to present it in due proportion I trust that a rule of polarisation has not clouded my judgment and established a bias in favour of this or that vibratory response to the inspirational work of the great men who have builded so well in this field of atomic physics.

In acknowledging my indebtedness to many sources, I would first mention Professor Arnold Sommerfeld, whose book has to me, in company with so many other students, been a fountain of philosophic ideas and scientific inspiration. To Professor Back I express my thanks for his kindness in placing at my disposal all the details of his experimental investigations of the Zeeman effect. To Professor Ornstein I express my deep sense of the honour he conferred upon me by writing an account of the Utrecht work on the measurement of lines of multiplets. Once again I thank the Editors and Proprietors of the *Astrophysical Journal* for their permission, so kindly given, to reproduce many illustrations from that journal. These are only four instances out of many. There remain numerous friends who have given me, possibly unknown to themselves, help of great value. Lastly, I record my earnest thanks to Miss E. E. Kelly, who in the preparation of this volume, as in that of the first two volumes, has given me real and valuable help which it is a pleasure to acknowledge.

E. C. C. BALY.

The University, Liverpool,
April, 1927.

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SPECTROSCOPY.

CHAPTER I.

SERIES OF LINES IN SPECTRA.

Rydberg's Work.—Of the older work on this subject there is no need to make mention, because, although certain regularities had been noticed, the first important work to come under our consideration is that by Balmer, who was the first to show that the lines of a spectrum could be expressed by a formula. This important discovery was made with the hydrogen elementary spectrum. Balmer [1] showed that the wave-lengths of the first nine lines of the hydrogen spectrum can be expressed by the equation

$$\lambda = h\frac{m^2}{m^2 - 4} \times 10^{-8} \text{ cm.},$$

where h is a constant and m is given the values 3, 4, 5, 6, etc., up to 11. The value of h was found to be 3645, and the calculated values of the wave-lengths of the lines agreed with the values actually measured within the limits of experimental error. As the number of hydrogen lines was extended into the ultra-violet from their discovery in the stars, and in the solar prominences and "flash" spectrum, and as their wave-lengths were better determined, it was found that Balmer's formula gave results which agreed in a most surprising way with those actually measured; proof was thus afforded that the wave-lengths are functions of successive whole numbers, that is to say, the lines of the hydrogen spectrum form a series, and the wave-lengths of any line can be expressed as a simple function of its number in the series. In order to show how accurately this formula expresses the measured wave-lengths, the measurements obtained by Evershed [2] from photographs of the solar eclipse of January 22, 1898, are given in Table I. The column headed "calculated" contains the values obtained from the formula of Balmer, in which h is put equal to 3646·13. The wave-lengths have been reduced to vacuum; the last column gives the differences between the observed and calculated values.

It can be seen at once from Balmer's formula that if m be put less than 3, indeterminate and negative values are obtained; and further, as m becomes larger the value of the coefficient $\frac{m^2}{m^2 - 4}$ becomes nearer

[1] *Ann. der Phys.*, **25**, 80 (1885).
[2] *Phil. Trans.*, **197**, A, 381 (1901), and **201**, A, 457 (1903).

TABLE I.

HYDROGEN SPECTRUM.

Designation.	Observed.	Calculated.	Difference.
α	6563·07	6563·03	+ 0·04
β	4861·57	4861·52	+ 0·05
γ	4340·53	4340·63	− 0·10
δ	4102·00	4101·90	+ 0·16
ϵ	3970·33	3970·22	+ 0·11
ζ	3889·15	3889·20	− 0·05
η	3835·51	3835·53	+ 0·02
θ	3798·00	3798·04	− 0·04
ι	3770·73	3770·77	− 0·04
κ	3750·27	3750·30	− 0·03
λ	3734·53	3734·51	+ 0·02
μ	3721·98	3722·08	− 0·10
ν	3712·13	3712·11	+ 0·02
ξ	3704·01	3704·00	+ 0·01
o	3697·28	3697·29	− 0·01
π	3691·70	3691·70	± 0·00
ρ	3686·96	3686·97	− 0·01
σ	3682·94	3682·95	− 0·01
τ	3679·52	3679·49	+ 0·03
υ	3676·51	3676·50	+ 0·01
ϕ	3673·87	3673·90	− 0·03
χ	3671·53	3671·48	+ 0·05
ψ	3669·55	3669·60	− 0·05
ω	3667·83	3667·82	+ 0·01
Series No. 27	3666·25	3666·24	+ 0·01
,, ,, 28	3664·74	3664·82	− 0·08
,, ,, 29	3663·55	3663·54	+ 0·01
,, ,, 30	3662·36	3662·40	− 0·04
,, ,, 31	3661·31	3661·35	− 0·04
,, ,, ∞	Theoretical limit.	3646·13	—

to unity, and therefore we may say that the end of the series ($m = \infty$) lies at $\lambda = h = 3646{\cdot}13$. It will be seen that as we advance in the series towards the ultra-violet the lines become nearer and nearer and nearer together, until the theoretical limit is reached. The agreement between the observed and calculated values, as will be seen, is extraordinarily close.

This observation made by Balmer has proved to be of fundamental importance. It led Rydberg on the one hand and Kayser and Runge on the other to a study of similar series of lines in other spectra. Then it was found as the result of Rydberg's pioneer work that relations of a simple nature exist between the various spectral series of one and the same element. Next came Ritz who made a great generalisation from Rydberg's advances in enunciating his combination principle which in its turn paved the way to the work of that great philosopher Bohr, who at one stroke revolutionised the whole subject by his outstanding conception of atomic structure. The year 1913 marked an epoch in spectroscopy, since all modern theory and practice in the

several fields of spectral series, in both line and band spectra, Zeeman effect and absorption spectra, may be said to have had their foundations laid at that time. The advances made in these fields, more particularly perhaps in the first two, have been of extraordinary interest and importance, and notably is this true of the last four years. The discovery in 1922 by Catalan of groups of lines in the spectra of manganese, more complex by far than any such that had previously been known, again marked a signal advance. It enabled Sommerfeld to remove the element of empiricism from his conception of inner quantum numbers and to weld the multiple field of spectral series with its new complexities into a well co-ordinated whole. To this unification Landé has contributed not a little and in his hands the Sommerfeld theory of the Zeeman effect has been extended until one is prepared to assert that so far as the simpler spectra are concerned the explanation is complete.

The task of writing an account of this work on spectral series and the Zeeman effect presents some difficulties for more than one reason. In the first place, the two fields are to a certain extent interconnected and this close relationship has become more and more pronounced until now the two march hand in hand. In spite of that the two have been kept separate with, I hope, sufficient cross references to serve as lines of communication. In the second place, two alternatives at once present themselves in any attempt to write on spectral series. One may, on the one hand, make a beginning with the Bohr epoch of 1913 and preface the chapter with an account of his theory, using just as little of previous knowledge as is required to explain it. This would then be followed by Sommerfeld's extension of the Bohr theory, again with the necessary illustrations from earlier experimental work. This would bring the reader right into modern work and the rest would be straightforward.

On the other hand, one may treat the subject as a whole and write a story of forty years' progress in this particular field, dealing with each advance, big or small, as far as possible in the order of its happening. I have ventured to choose this alternative and offer some reasons for my choice, though these perhaps are of a personal nature. I believe myself that the first alternative would lead possibly to a wrong perspective as regards the relation of theory to experiment, for I maintain that in this field of spectroscopy theory has in the main waited on experiment, the most notable exception being the modern work on enhanced line spectra. Then again I would confess to finding a touch of romance in the story as a whole, and it is not good to start off such a story with mathematical formulæ, the elegance of which to my mind does not justify so early an intrusion on their part. Furthermore, let there be honour where honour is due, and the names of Rydberg, Kayser, Runge, Paschen, Fowler, Millikan, and many others are written large on the pages of this history of ours, and I would that their works be appreciated. Lastly, may I attempt to parry criticism of my choice by expressing a belief that there seems

as yet to have been no attempt made to tell the whole story, so perhaps the following may not come too much amiss.

It is a long step from Balmer's first publication in 1885 of his arrangement of the first nine lines of the hydrogen spectrum into a series expressed by a simple formula to our present-day knowledge of similar series, each term of which consists not of one single line but of many lines, some terms being composed of as many as fifteen lines all connected together by definite relationships. The foundation of our present knowledge is to be found in the work of Rydberg and also in that of Kayser and Runge, though the latter, as events have proved, contributed to this foundation in a somewhat different way. Both Rydberg on the one hand and Kayser and Runge on the other showed that the lines in the spectra of many other elements can be grouped in series which can be expressed by formulæ analogous to but not quite so simple as that of Balmer. Kayser and Runge discovered many such series and showed that they all could be expressed by formulæ of the same type, the constants of which varied from series to series and from element to element. Rydberg concerned himself with the expression of series by one single formula with constants characteristic of each series type and the relations between the different series given by one element. The formula of Kayser and Runge has died a natural death, whilst that of Rydberg is still used as a valuable help in the preliminary work of assigning the lines to their appropriate series. The work of Kayser and Runge in raising the standard of spectroscopic measurement played a very important rôle in these early days of our story.

We will take up the story at the time when Rydberg began to publish the results of his calculations.

Rydberg published a full description of how he obtained his formula, and the results of its application to known results, in the *Transactions of the Royal Swedish Academy* in 1890.[1] Runge,[2] in 1888, stated that he had discovered a number of harmonic series in the spectra of certain elements, and that these can be expressed by a formula of the type

$$\frac{1}{\lambda} = a + \frac{b}{n} + \frac{c}{n^2} \text{ or } \frac{1}{\lambda} = a + \frac{b}{n^2} + \frac{c}{n^4}.$$

Balmer's formula may be looked upon as a specially simple case of the above; for, instead of

$$\lambda = h\frac{m^2}{m^2 - 4}$$

we may put

$$\frac{1}{\lambda} = \mathrm{A}\frac{m^2 - 4}{m^2}, \text{ where } \mathrm{A} = \frac{1}{h},$$

and

$$\frac{1}{\lambda} = \mathrm{A} + \frac{\mathrm{B}}{m^2}, \text{ where } \mathrm{B} = -4\mathrm{A}.$$

[1] *K. Svenska Vetensk. Akad. Hand.*, Vol. XXIII., No. 11 (1890).
[2] *Brit. Ass. Report* (1888), 576.

Rydberg, however, claimed to have been using his formula before 1885, when Balmer's was first published.

Rydberg has given a very complete description of how he arrived at his formula in the paper above referred to, and it is necessary to discuss this work very fully in order to understand the extremely interesting results he obtained in the connection between the various series of lines belonging to the same element as well as the actual expression of the lines in series.

Two very important observations, one by Hartley and the other by Liveing and Dewar, must first be mentioned. It had long been known that in the spectra of certain elements other than hydrogen the lines could obviously be grouped in pairs or in triplets. The spectra of the alkali metals, sodium and potassium, were known to be characterised by pairs of lines or doublets, whilst the spectra of the alkaline earth metals, magnesium, zinc, and cadmium, were known to be characterised by the triplet grouping of the lines.

In the first place, Hartley [1] found that if the lines in a spectrum are expressed in wave-numbers and not in wave-lengths, then the differences between the components of the doublet or triplet are the same for all the doublets or triplets in the same spectrum. Hartley only examined the triplets in the spectra of magnesium, zinc, and cadmium, and as an example three triplets of the zinc spectrum are set forth in Table II., the wave-numbers being given to four figures only :—

TABLE II.

			Diff.		Diff.	
1		2079	910	2989	582	3571
	Diff.	39		39		38
2		2118	910	3028	581	3609
	Diff.	18		18		20
3		2136	910	3046	583	3629

The numbers 1, 2, and 3 refer to the first, second, and third members of the triplets ; it will be seen that the difference between the first and second member is about 39, and between the second and third it is about 18.

The second discovery, by Liveing and Dewar,[2] was that of the existence of homologous series of lines, that is to say series of lines of the same type in chemically analogous elements, although they did not find the law of the series. They established also the existence of a series of lines which are sharp, and a similar series of diffuse lines.

Rydberg calculated the wave-numbers of the observed lines in a great number of elementary spectra, and selected the doublets and triplets of constant wave-number difference. It should be pointed out that, as the accuracy of the measurements he dealt with were great compared with the accuracy of the determination of the index of

[1] *Chem. Soc. Trans.*, **43**, 390 (1883).
[2] *Phil. Trans.*, **174**, 187 (1883).

refraction of air as known at that time, they were not reduced to vacuum. As regards the doublets and triplets, these may often be recognised by the eye, but often the components are very far removed from one another, there being a considerable number of lines in between them. The names of doublet and triplet might be thus considered as rather misnomers, were they not defined in the first place as pairs or trios of lines with a constant wave-number difference. In speaking of these differences in wave-number, for simplicity's sake we will use Rydberg's notation for the present, and speak of the wave-number difference of a doublet as ν, and that between the first two and second two members of a triplet as ν_1 and ν_2. Further, the component of a doublet or triplet with the smallest wave-number is called n_1, and the next in order of magnitude n_2, and the third member (of a triplet) n_3; we therefore have

$$\nu = n_2 - n_1 \text{ with a doublet,}$$

and $\nu_1 = n_2 - n_1$

and $\nu_2 = n_3 - n_2$ } with a triplet.

As was said before, Rydberg calculated the wave-numbers of the known lines of a number of elements, and selected the doublets and triplets of constant wave-number difference therefrom. Then, assuming that analogous lines of a spectrum are functions of a series of consecutive whole numbers, or, in other words, that the analogous lines form a simple series, he attempted to find the graphical relation between the lines. He placed the wave-lengths upon the ordinates and the numbers of the lines in the series on the abscissæ, calling the least refrangible of the analogous lines number 1. In this way he obtained for the doublet and triplet series two or three curves, which became parallel to one another when wave-numbers were used instead of wave-lengths.

If now we consider the case of sodium and take the least refrangible lines of the doublets, we then have, on Ångström's scale,

m	λ	m	λ	m	λ
1	8199	5	5155·0	9	4543·6
2	6160	6	4983·0	10	4496·4
3	5895	7	4751·4	11	4423·0
4	5687	8	4667·2	12	4393·0

where m is the order or number of the rays. On plotting these numbers Rydberg found that they did not form a regular curve, but that the points lay first on the one side and then on the other side of a mean curve; this anomaly disappeared entirely when the line at $\lambda = 5895$ was suppressed, and the remaining lines were taken alternately to form two series, thus :—

m	1	2	3	4	5	6
λ_1	8199	5687	4983·0	4667·2	4496·4	4393
λ_2	6160	5155	4751·4	4543·6	4423·0	

Now, as each of these lines is the component of a doublet, we have evidently two series of pairs, or four series of lines. It is most important to remember that Liveing and Dewar observed all these lines, and found that those in the upper line are all diffuse, and that those in the lower line are sharp, so that one could distinguish between the two series independently of the curves just described.

It was found on comparing the curves together that they all had the same general shape, and therefore Rydberg concluded that they could all be expressed by a common formula. As the curves appeared to approximate to rectangular hyperbolas, Rydberg first took the formula

$$(\lambda - \lambda_0)(m + \mu) = \text{constant, in wave-lengths,}$$

or $$(n - n_0)(m + \mu_1) = C_1, \text{ in wave-numbers,}$$

where λ_0, μ and n_0, μ_1 are constants.

Rydberg then calculated the wave-lengths from this formula,

$$\lambda = \lambda_0 + \frac{C}{m + \mu},$$

and found that very fair approximations to the measured values were obtained. Rydberg satisfied himself in this way that the wave-lengths and wave-numbers of a series of analogous lines in the spectrum of an element are functions of a series of consecutive whole numbers.

Rydberg next considered the differences between the wave-numbers of the successive members of the series, and he found that these differences (Δn) become smaller as one goes higher into the series; this, of course, naturally follows from the fact that the lines of a series get closer together as one advances in the series. The values of Δn were calculated for all the series which could be recognised, and Rydberg obtained in this way series of decreasing values of Δn, one series for each naturally occurring series of spectral lines. Each of these series of values of Δn seemed to be perfectly comparable, so that when these values were arranged according to the magnitude of any term, all the other terms followed one another in the same order of magnitude. This can be best explained by means of Table III., which was given by Rydberg of the values of Δn obtained by him.

In the first column are given the symbols of the elements and the designation of the series, which will be explained later. The second column contains the differences between the wave-numbers of the first and second terms of the series given, the third column contains the wave-number differences between the second and third members, and so on. In Table III. the series are so arranged that the wave-number differences in the second column form a descending scale in order of magnitude; this was done because all the terms of the second column were not known. It will be seen that with very few exceptions all the terms in the other columns are arranged in descending order of magnitude, and further, that the first term of each column is smaller

than the last term of the preceding column. Rydberg also expressed these results as follows: The differences between the corresponding terms of any two series of values of Δn have the same sign.

TABLE III.

VALUES OF Δn.

Name of Series.	Between $m = 1$ and $m = 2$.	Between $m = 2$ and $m = 3$.	Between $m = 3$ and $m = 4$.	Between $m = 4$ and $m = 5$.	Between $m = 5$ and $m = 6$.	Between $m = 6$ and $m = 7$.	Between $m = 7$ and $m = 8$.	Between $m = 8$ and $m = 9$.
Li (P_{12})	16026·8	5542·4	2556·6	1364·4	824·6	533·8	369·5	258·9
Na (D_1)	—	5386·7	2484·9	1357·9	813·9	523·5	—	—
Ca (D_1)	—	4996·7	2323·9	1246·3	723·4	—	—	—
Na (P_1)	13314·9	4751·4	2280·2	1233·5	—	—	—	—
Tl (S_2)	12278·3	4395·1	2089·6	1213·0	732·4	465·6	350·1	250·2
K (P_1)	11685·9	4303·8	2050·3	1158·0	723·0	451·8	322·5	245·5
Mg (S_1)	10679·5	4017·2	1957·5	1116·5	685·6	—	—	—
Ca (S_1)	8943·7	3507·8	1759·3	1015·0	620·6	—	—	—
Na (S_1)	7484·8	3165·6	1647·0	962·6	600·1	407·6	—	—
K (D_1)	—	2842·7	1507·5	881·2	550·5	385·8	256·9	—
Mg (D_1)	6241·8	2775·3	1476·7	868·4	561·4	—	—	—
Zn (D_1)	5812·3	2636·4	1416·8	862·7	—	—	—	—

The next step taken by Rydberg was to plot the values of Δn as given in Table III. against the series of whole numbers (m) 1, 2, 3, etc.; the curves obtained in this way all had the same shape, so that it seemed probable that they could be made to coincide with one another throughout their length by simply shifting them parallel to the axis of m. This we can express by saying that if Δn is a function of m for one curve, then the general equation to all the curves is

$$\Delta n = \mathrm{F}(m + \mu),$$

where μ is a constant. From this Rydberg derived the equation for a spectral series,

$$n = n_0 - f(m + \mu),$$

where n is the wave-number, n_0 is a constant, and $f(m + \mu)$ some function of $(m + \mu)$, which has the same form and the same constants for every member in every series.[1]

[1] PROOF—

$$\begin{aligned} n_m &= n_{m+1} - \Delta n \\ n_m &= n_{m+1} - \mathrm{F}(m + \mu) \\ n_{m+1} &= n_{m+2} - \mathrm{F}(m + 1 + \mu) \\ n_{m+2} &= n_{m+3} - \mathrm{F}(m + 2 + \mu) \end{aligned}$$

Now, we know that n approaches a limit n_0 when $m = \infty$, and the form of the

If we put $f(m + \mu) = \frac{C}{m + \mu}$ we have the equation

$$n = n_0 - \frac{C}{m + \mu}.$$

We have already seen that a very similar equation,

$$\lambda = \lambda_0 + \frac{C}{m + \mu},$$

expresses a series with a very rough approximation. Considering the shape of the curves already described, obtained by plotting λ against m, the next simplest equation is

$$n = n_0 - \frac{N}{(m + \mu)^2},$$

where N is another constant.

This equation Rydberg found to answer extraordinarily well, and is the equation he finally adopted; in it N is a constant for all series and all substances, n_0 is the value of n when $m = \infty$, that is to say, it is the theoretical limit of the series, and is sometimes known as the convergence limit, and μ is a characteristic constant of the element and the series.

Now, Balmer's hydrogen equation may be considered as a special case of this formula, for if instead of his equation for the wave-length

$$\lambda = h\frac{m^2}{m^2 - 4}$$

we put

$$n = n_0\frac{m^2 - 4}{m^2},$$

when

$$n = \frac{10^8}{\lambda} \quad \text{and} \quad n_0 = \frac{10^8}{h}$$

then we have

$$n = n_0 - \frac{4n_0}{m^2},$$

series of Δn and the shape of the corresponding curves leads us to suppose that the limit of Δn or $F(m + \mu) = 0$ when $m = \infty$; we have, therefore,

$$n_m = n_0 - \sum_m^\infty F(m + \mu).$$

For another series we have

$$n'_m = n'_0 - \sum_m^\infty F(m + \mu').$$

Now, the two sums which enter into these equations have the same number of terms, and we know that any term in one of the sums only differs from the corresponding term in the other by the value of the constant μ; then one of the sums is changed into the other if μ is changed to μ', whence it follows that there are only two different values of the same function of μ.

Next, putting

$$\sum_m^\infty F(m + \mu) = f(m + \mu),$$

we have the general equation

$$n = n_0 - f(m + \mu).$$

which equation is evidently the same as Rydberg's general equation, if N in the latter $= 4n_0$ and $\mu = 0$.

In making use of the formula

$$n = n_0 - \frac{N}{(m + \mu)^2},$$

it must be remembered that Rydberg did not claim that it reproduces the measurements of the wave-numbers of lines with absolute accuracy —he recognised that it is only a very near approximation to the true relations. In comparing the observed wave-numbers and those calculated by means of this formula, and by means of the formula of Kayser and Runge, no one could deny that the agreement was often better in the second case. Kayser and Runge's formula expresses a series of lines sometimes with extraordinary accuracy, but there its use ceases, whereas Rydberg by means of his formula was able to trace the connection between the different series, and even to calculate the wave-lengths of the lines of one series from the equation to another series.

The method used by Rydberg in calculating the constants of his formula may now be described. He determined the value of the universal constant N once and for all from the Balmer formula for hydrogen which may be written in the form

$$h = \lambda \frac{m^2 - 4}{m^2}.$$

In calculating the value of h, Rydberg used the old values of the wave-lengths of the hydrogen lines as follows :—

$$\begin{aligned} h &= 6562{\cdot}10 \times \tfrac{5}{9} = 3645{\cdot}611 \text{ for } m = 3 \\ h &= 4860{\cdot}74 \times \tfrac{3}{4} = 3645{\cdot}555 \text{ for } m = 4 \\ h &= 4340{\cdot}10 \times \tfrac{2}{2}\tfrac{1}{5} = 3645{\cdot}684 \text{ for } m = 5 \\ h &= 4101{\cdot}20 \times \tfrac{8}{9} = 3645{\cdot}510 \text{ for } m = 6 \\ &\text{Mean} = 3645{\cdot}590 \end{aligned}$$

From this

$$N = \frac{4 \times 10^8}{3645{\cdot}590} = 109721{\cdot}6.$$

From later measurements of the wave-lengths of the hydrogen lines, Rydberg found the value of this constant to be 109675·00 which he used in all his later work. The constants n_0 and μ are characteristic of each element and each series and therefore must be found for each. In the early days of Rydberg's work this was very much more laborious than it is at the present time owing to the fact that the measurements of spectrum lines were relatively inaccurate. The method Rydberg used may be indicated by the sharp series of magnesium which consists of triplets with constant wave-number difference. In the first place, as many of the triplets as possible were picked out from the whole spectrum and the values of the wave-number differences ν_1 and ν_2 found. The mean values of ν_1, ν_2 and $\nu_1 + \nu_2$

were obtained from these, and with the help of these mean values the wave-numbers of all the second and third members of the triplets were reduced to the scale of the first members. In this way three values for the first member of each term are found, and the mean of these three in each case gives a far closer approximation to the true wave-number of the first member of each term than the measured value. The measured values are given in Table IV.

TABLE IV.

SHARP SERIES OF MAGNESIUM.

	m	2	3	4	5	6	7
S_1	. .	19293·8	29973·3	33990·5	35948·0	37064·5	37750·1
		41·1	40·5	40·5	40·0	42·3	42·8
S_2	. .	19334·9	30013·8	34031·0	35988·0	37105·8	37792·9
		19·8	24·4	11·6	23·4	20·6	—
S_3	. .	19354·7	30038·2	34042·6	36011·4	37126·4	—

From these the mean values of ν_1, ν_2 and $\nu_1 + \nu_2$ are found to be 41·4, 20·6, and 62·0 respectively, and thus all the observations may be reduced to the scale of S_1 as shown in Table V.

TABLE V.

S_1 obs. .	19293·8	29973·3	33990·5	35948·0	37064·5	37750·1
S_1 calc. .	19293·5	29972·4	33989·6	35946·6	37064·4	37751·5
S_1 calc. .	19292·7	29976·2	(33990·6)	35949·4	37064·4	—
Means	19293·3	29974·0	33990·1	35948·0	37064·4	37750·8

The last row of means in Table V. is adopted as the best value of the wave-numbers of the first members of the triplets. It may be noted that since ν_1, ν_2 are the differences between the first and second and the second and third members of the triplets, the equations for the three members are the same, except that the value of n_0 differs in each case by the amounts ν_1 and ν_2.

For the determination of the value of μ it will be obvious that since m in Rydberg's formula has successive integral values, μ must lie between 0 and 1. The simplest way to find μ is by means of an interpolation table and Rydberg gave such a table containing all the values of $109721{\cdot}6/(m+\mu)^2$ for all the values of m from 1 to 9, and all the values of μ from 0·00 to 1·00 differing by 0·01.[1] The table also included the values of Δn, or differences between every two successive values of $109721{\cdot}6/(m+\mu)^2$ formed by increasing m to $m+1$.

In using this table for the finding of μ, first of all the values of Δn for the series are found, and as an example the series of thallium may be quoted as given by Rydberg, and the data are set forth in Table VI.

[1] This table is reproduced on p. 300, the values being recalculated with the most recent value of N, namely, 109678·3.

TABLE VI.

λ	n	Δn	m
3517·8	28426·9		
		5845·5	2
2917·8	34272·4		
		2644·3	3
2708·8	36916·7		
		1418·0	4
2608·6	38334·7		
		850·3	5
2552·0	39185·0		
		544·8	6
2517·0	39729·8		7

From Table VI. we find that the difference in the value of $\frac{N}{(m+\mu)^2}$,

1. When $m = 2$ and $m = 3$ is 5886·2 for $\mu = 0{\cdot}89$ and 5832·8 for $\mu = 0{\cdot}90$
2. When $m = 3$ „ $m = 4$ „ 2662·3 „ $\mu = 0{\cdot}89$ „ 2644·0 „ $\mu = 0{\cdot}90$
3. When $m = 4$ „ $m = 5$ „ 1425·9 „ $\mu = 0{\cdot}89$ „ 1417·8 „ $\mu = 0{\cdot}90$
4. When $m = 5$ „ $m = 6$ „ 851·4 „ $\mu = 0{\cdot}89$ „ 847·4 „ $\mu = 0{\cdot}90$
5. When $m = 6$ „ $m = 7$ „ 548·8 „ $\mu = 0{\cdot}89$ „ 544·3 „ $\mu = 0{\cdot}91$

Evidently the value of μ is given by 1. as $0{\cdot}89 + \frac{40{\cdot}7}{53{\cdot}4} \times {\cdot}01$, by 2. as $0{\cdot}89 + \frac{18}{18{\cdot}3} \times 0{\cdot}01$, by 3. as $0{\cdot}89 + \frac{7{\cdot}9}{8{\cdot}1} \times 0{\cdot}01$, by 4. as $0{\cdot}89 \times \frac{1{\cdot}1}{4{\cdot}0} \times 0{\cdot}01$, and by 5. as $0{\cdot}89 + \frac{4}{4{\cdot}5} \times 0{\cdot}02$.

Now, in finding the mean of all the fractions thus given Rydberg weights the values according to the square of the wave-length of the lines; these fractions are, respectively, multiplied by 100, 73, 68, 65, 63, which are the relative weights to be given, then all the numerators are added together and divided by the sum of all the denominators. In this way the mean comes out to 0·0082, and thus the value of μ is found to be 0·8982.

We have, finally, to find the constant n_0, which may be done as follows:

Writing the equation

$$n_0 = n + \frac{N}{(m+\mu)^2},$$

the value of n_0 can at once be found for all the analogous lines of the series, and their mean is adopted as n_0. To take an example, the above given values may be used of thallium, for which we have found that

$$n_0 = n + \frac{109721{\cdot}6}{(m + 0{\cdot}8982)^2}.$$

The values of the last term are calculated for $m = 2$, 3, 4, etc., since these are the numbers of the lines in the series as given above; to the values thus obtained the corresponding wave-number n is added, and thus as many determinations of n_0 are obtained as there are lines in the series. These values are weighed as before described according to λ^2, and the mean is then adopted as the constant; in this case its value was found to be 41490·2.

The complete equation is, therefore,

$$n = 41490{\cdot}2 - \frac{109721{\cdot}6}{(m + 0{\cdot}8982)^2}.$$

Relation between the Series belonging to One Element.—Reference has already been made to the existence in the case of elements other than hydrogen of two series, the sharp and nebulous series, which consist of doublets or triplets of constant wave-number difference. It may therefore be stated that each element possesses two or three sharp series parallel to one another, and the same number of diffuse series also parallel to one another, and the wave-number differences of corresponding rays are constant for each element. If, then, n_1, n_2, and n_3 represent the values of the constant n_0 for each of the sharp or nebulous series, we have

$$n = n_1 - \frac{N}{(m + \mu)^2},$$
$$n = n_2 - \frac{N}{(m + \mu)^2},$$
$$n = n_3 - \frac{N}{(m + \mu)^2},$$

and $n_2 - n_1 = \nu$ in the doublet series, and in the triplet series $n_2 - n_1 = \nu_1$ and $n_3 - n_2 = \nu_2$. There are thus four or six series with each element, and Rydberg calls them the first, second, or third sharp or nebulous series as the case may be. The three sharp series form the sharp group, and similarly we have the nebulous group.

Now Rydberg found that the value of the constant n_0 is the same for the corresponding sharp and nebulous series. In other words, the convergence limits of the corresponding series are the same in the sharp and nebulous groups. If, therefore, we write δ for μ in the equation for the diffuse series, and σ for μ in the sharp series, we have the equations—

Sharp Group.	Nebulous Group.	
$n = n_1 - \frac{N}{(m + \sigma)^2}$	$n = n_1 - \frac{N}{(m + \delta)^2}$	First series.
$n = n_2 - \frac{N}{(m + \sigma)^2}$	$n = n_2 - \frac{N}{(m + \delta)^2}$	Second series.
$n = n_3 - \frac{N}{(m + \sigma)^2}$	$n = n_3 - \frac{N}{(m + \delta)^2}$	Third series.

These equations show fully the connection between the six series. In the case of the alkali metals the sharp and nebulous series consist of doublets and it had been found that in these spectra there existed another series of doublets. These series were called by Rydberg the principal series, because they contained the most intense lines in the spectra of these elements. At that time the principal series

had only been recognised in the alkali metal spectra, though Rydberg later found them in the spectra of other elements.

These principal series differ materially from the sharp and nebulous series in that they consist of pairs which have not a constant wave-number difference, for the components of each pair get closer together as the order number rises. Evidently, therefore, the two series should have the same convergence limit, for, since as m gets larger the pairs come closer together, therefore at the limit when $m = \infty$ they should be an infinitely small distance apart. This is experimentally borne out by the values of n_0 actually obtained. The more refrangible line of the pairs is always the stronger line, so that Rydberg calls the series of less refrangible lines the weak, and the other the strong, principal series. The equations are as follows :—

$$n = n_0 - \frac{N}{(m + \mu_1)^2},$$

$$n = n_0 - \frac{N}{(m + \mu_2)^2}.$$

The connection between the principal series and the sharp series is exceedingly interesting and important. Rydberg found that in the case of sodium, potassium, and rubidium the wave-number difference between the members of the first pair of the principal series was almost exactly equal to the constant wave-number difference of the pairs of the sharp and nebulous series. We may therefore put

$$\nu = n_0 - \frac{N}{(m + \mu_1)^2} - \left\{ n_0 - \frac{N}{(m + \mu_2)^2} \right\},$$

whence

$$\nu = \frac{N}{(m + \mu_2)^2} - \frac{N}{(m + \mu_1)^2}.$$

Rydberg, however, found a very close relation between the sharp and principal series, namely, that they are both parts of the same series with two variables. He arrived at it in this way : In the case of lithium the pairs which exist in the spectrum are very close together and very difficult to resolve,[1] so that we need only consider three series—the principal, sharp, and nebulous series—each term of which is in reality a close pair. Now, Rydberg found for the sharp series of lithium

$$n = 28601 - \frac{109721 \cdot 6}{(m + 0 \cdot 5951)^2},$$

and for the principal series

$$n = 43487 \cdot 7 - \frac{109721 \cdot 6}{(m + 0 \cdot 9596)_2},$$

[1] Kent has succeeded in resolving five of the lithium lines by means of an echelon grating. *Astrophys. Journ.*, **40**, 337 (1914).

where $m = 2, 3, 4$, etc., for the sharp series, and 1, 2, 3, etc., for the principal series. The value $m = 1$ in the first equation gives a negative value of n because the expression $\frac{109721{\cdot}6}{(m + 0{\cdot}5951)^2}$ then equals 43123·7. Now this number is not far from the constant 43487·7 of the principal series equation; again, putting $m = 1$ in the second equation, then

$$\frac{109721{\cdot}6}{(m + 0{\cdot}9596)^2} = 28573{\cdot}1,$$

a number very close to the constant 28601 of the sharp series equation. Within a close approximation, then, we may write for the principal series

$$\frac{n}{N} = \frac{1}{(1 + 0{\cdot}5951)^2} - \frac{1}{(m + 0{\cdot}9596)^2},$$

and for the sharp series

$$\frac{n}{N} = \frac{1}{(1 + 0{\cdot}9596)^2} - \frac{1}{(m + 0{\cdot}5951)^2}.$$

Or, more generally,

$$\frac{n}{N} = \frac{1}{(1 + \mu)^2} - \frac{1}{(m + \sigma)^2} \text{ for the sharp series,}$$

and

$$\frac{n}{N} = \frac{1}{(1 + \sigma)^2} - \frac{1}{(m + \mu)^2} \text{ for the principal series.}$$

Putting $m = 1$ in both equations we obtain the same numerical values of n, but the value obtained from the sharp series equation is negative. The first term of the sharp series is the same as the first term of the principal series; in this case the red ray of lithium $\lambda = 6708$. Referring again to the equation for the principal series of lithium given above, and putting $m = 1$,

$$n = 43487{\cdot}7 - \frac{109721{\cdot}6}{(1 + 0{\cdot}9596)^2},$$

but $\frac{109721{\cdot}6}{(1 + 0{\cdot}9596)^2}$ has already been shown to be equal to 28573·1, which is the constant n_0 of the sharp series. In other words, the difference between the convergence limits of the principal and sharp series is equal to the wave-number of the first line of the principal series. This relation was later discovered independently by Schuster, and is generally known as the Rydberg-Schuster law.

These relations are very important for several reasons. In the first place, it is possible to calculate the whole of the principal series from the sharp series as follows:—

The sharp series equation is

$$n = n_0 - \frac{N}{(m + \sigma)^2}.$$

Putting $m = 1$ we get the negative value of n, which is the first line of the principal series; further, the value of $\frac{N}{(1+\sigma)^2}$ is the convergence limit of the principal series. From these two terms the rest of the calculation is easy.

One point more about this connection between the two series; in the alkali metal series each of the terms is a pair, so we therefore have two equations for the principal, and two for the sharp series:—

$$\left.\begin{array}{ll} (1) & \frac{n}{N} = \frac{1}{(1+\sigma)^2} - \frac{1}{(m+\mu_1)^2} \\ (2) & \frac{n}{N} = \frac{1}{(1+\sigma)^2} - \frac{1}{(m+\mu_2)^2} \end{array}\right\} \text{Principal series.}$$

$$\left.\begin{array}{ll} (1) & \frac{n}{N} = \frac{1}{(1+\mu_1)^2} - \frac{1}{(m+\sigma)^2} \\ (2) & \frac{n}{N} = \frac{1}{(1+\mu_2)^2} - \frac{1}{(m+\sigma)^2} \end{array}\right\} \text{Sharp series.}$$

It is a natural consequence of what has gone before that the two series correspond in such a way that the more refrangible line in the case of the first is analogous to the less refrangible line of the second, and *vice versa*. This can readily be seen from the equations; let us put $\mu_1 > \mu_2$, then evidently equation (1) of the sharp series refers to the component lines of the pairs which have the smaller wave-number, *i.e.* the less refrangible line of the pairs, whilst equation (2) refers to the more refrangible line. Putting $m = 1$, then clearly equation (1) of the principal series (which is analogous to equation (1) of the sharp series) will refer to the lines with larger wave-number, and equation (2) of the principal series refers to the less refrangible lines. The conditions in the principal series are reversed, so to speak, from what they were in the sharp series. This is shown very clearly by the relative brightness of the component lines in the pairs of the two series; for example, in the principal series of the alkali metals the more refrangible component of the pairs is the brighter in each case; in the sharp series it is the less refrangible line which is the brighter. It is more strikingly, perhaps, shown by means of the Zeeman effect. In Chapter II., p. 312, it will be shown how the principal series shows two types of resolution, one for the more refrangible line of each pair, and one for the less refrangible line; the same types exactly are shown by the sharp series, but in the reverse order, that is to say, the type of D_1, as it is called, is shown by the more refrangible line of the pair, and the type of D_2 by the less refrangible line.

Rydberg also dealt with another series, one which is attendant on the nebulous series. He was only able to recognise it in the case of thallium, but quite rightly presumed its existence with other elements; it occurs as a series of satellites accompanying the nebulous series. In this series the wave-number difference between these lines and the corresponding line of the nebulous series itself decreases with

increase of m. The secondary series have, therefore, the same convergence limit as the nebulous series proper.

We may now give in Table VII. the complete scheme for the whole spectrum of an element showing triplets. In this table $\mu_1 > \mu_2 > \mu_3$.

TABLE VII

NEBULOUS GROUP.

1st nebulous series	$\frac{n}{N} = \frac{1}{(1+\mu_1)^2} - \frac{1}{(m+\delta')^2}$	D'_1
2nd " "	$\frac{n}{N} = \frac{1}{(1+\mu_2)^2} - \frac{1}{(m+\delta')^2}$	D'_2
3rd " "	$\frac{n}{N} = \frac{1}{(1+\mu_3)^2} - \frac{1}{(m+\delta')^2}$	D'_3

SECONDARY GROUP (NEBULOUS).

1st secondary series	$\frac{n}{N} = \frac{1}{(1+\mu_1)^2} - \frac{1}{(m+\delta'')^2}$	D''_1
2nd " "	$\frac{n}{N} = \frac{1}{(1+\mu_2)^2} - \frac{1}{(m+\delta'')^2}$	D''_2
3rd " "	$\frac{n}{N} = \frac{1}{(1+\mu_3)^2} - \frac{1}{(m+\delta'')^2}$	D''_3

SHARP GROUP.

1st sharp series	$\frac{n}{N} = \frac{1}{(1+\mu_1)^2} - \frac{1}{(m+\sigma)^2}$	S_1
2nd " "	$\frac{n}{N} = \frac{1}{(1+\mu_2)^2} - \frac{1}{(m+\sigma)^2}$	S_2
3rd " "	$\frac{n}{N} = \frac{1}{(1+\mu_3)^2} - \frac{1}{(m+\sigma)^2}$	S_3

PRINCIPAL GROUP.

1st principal series	$\frac{n}{N} = \frac{1}{(1+\sigma)^2} - \frac{1}{(m+\mu_1)^2}$	P_1
2nd " "	$\frac{n}{N} = \frac{1}{(1+\sigma)^2} - \frac{1}{(m+\mu_2)^2}$	P_2
3rd " "	$\frac{n}{N} = \frac{1}{(1+\sigma)^2} - \frac{1}{(m+\mu_3)^2}$	P_3

There are thus twelve equations, which contain only six constants, if we do not include N, which is the same for every series and substance.

In speaking of any line Rydberg uses the symbols given above

for the series, and puts the number of the line in its series. Thus Cd [D] means all the lines of the nebulous group of cadmium, including the primary Cd [D′] and the secondary Cd [D″]. Again, Na [P_1 . 1] means the first line of the first principal series of sodium, which is the D_2 line, because the first principal series contains the lines of the pairs which have the greater wave-number; this is due to the fact that Rydberg views the principal series as really part of the sharp series. Similarly, Rb [S_2 2] is the second line of the second sharp series of rubidium; it will be remembered that the first line is the first line of the second principal series.

Rydberg at a later date applied his theory of the relation between the three series systems of an element to the interpretation of the origin of certain lines found in the spectra of stars and nebulæ. He showed that these lines could be attributed to hydrogen, and the result of this reasoning led to great confidence being placed in Rydberg's theory.

As already explained the well-known elementary spectrum of hydrogen is very accurately expressed by Balmer's formula which can be written in the same form as Rydberg's formula, thus :—

$$n = 27418{\cdot}75 - \frac{109675{\cdot}00}{(m+1)^2}$$

where $m = 2, 3, 4,$ etc.

Now, in 1896, Pickering [1] discovered in the spectrum of the star ζ Puppis, which shows the hydrogen spectrum strongly, a new series of lines which is very analogous to the known hydrogen spectrum. Indeed, Pickering showed that their wave-lengths could be expressed by the modified Balmer's formula

$$\lambda = 4650\frac{m^2}{m^2 - 4} - 1032.$$

In a further publication Pickering [2] united both the series to one formula as follows: he put $m = \frac{n}{2}$ in the usual Balmer formula, and thus obtained

$$\lambda = 3646{\cdot}1\frac{n^2}{n^2 - 16}$$

where $n = 6, 8, 10, 12,$ etc. He then found that the new series was obtained by putting $n = 11, 13, 15, 17,$ etc.

Now, Kayser [3] at once pointed out that there are serious reasons against uniting these two series into one; among these may be asked —if they all belong to one series, why do we always in terrestrial spectra see only the half of the series?

Rydberg [4] brought more conclusive evidence forward in favour

[1] *Astrophys. Journ.*, **4**, 369 (1896).
[2] *Ibid.*, **5**, 92 (1897).
[3] *Ibid.*, **5**, 243 (1897).
[4] *Ibid.*, **6**, 233 (1897).

of Kayser's views. He first of all showed that the two series have the same convergence limit, and then found that the equation for the second series was as follows :—

$$n = 27418{\cdot}75 - \frac{109765{\cdot}00}{(m + 0{\cdot}500737)^2},$$

whence he obtained the values at 16° and 760 mm. in air, shown in Table VIII.

TABLE VIII.

m	5	6	7	8	9	10
λ obs. .	4201·6	4026·5	3924·9	3858·6	3817·2	3783·4
λ calc. .	4201·54	4027·31	3925·18	3859·76	3815·17	3783·35
Diff. .	+ 0·06	− 0·81	− 0·28	− 1·16	+ 2·03	+ 0·05

The two series thus behave like the nebulous and sharp series of hydrogen, and in terms of the general Rydberg formulæ for the series system of an element giving single lines, the equations can be written in the form—

$$\text{Nebulous series, } n = \frac{N}{(1+1)^2} - \frac{N}{(m+1)^2} \qquad m = 2, 3, 4, \text{ etc.}$$

$$\text{Sharp series, } n = \frac{N}{(1+1)^2} - \frac{N}{(m+0{\cdot}5)^2} \qquad m = 2, 3, 4, \text{ etc.}$$

From the Rydberg-Schuster law we may at once derive from these the equation for the principal series of hydrogen, which will be

$$n = \frac{N}{(1+0{\cdot}5)^2} - \frac{N}{(m+1)^2}, \text{ where } m = 1, 2, 3, \text{ etc.}$$

From this equation Rydberg calculated the wave-lengths of the lines in the principal series of hydrogen and these are given in Table IX.

TABLE IX.

m	1	2	3	4	5
n	21325·69	36558·33	41889·75	44357·44	45697·91
λ	4687·88	2734·55	2386·50	2253·74	2187·60

The values of n are for vacuum, but those of λ have been reduced to air at 16° and 760 mm. in order to enable a comparison with observed values. Rydberg pointed out that this series of lines should be exhibited by hydrogen and might appear in stellar spectra. Owing, however, to the effect of atmospheric absorption only the first line of the series will be visible and this line, if seen, ought to be exceptionally brilliant, like the red line of lithium and the D lines of sodium. As a matter of fact there has been found in the spectra of several stars a strong line at $\lambda = 4688$ which clearly is the first line of Rydberg's series. Moreover, Hale and Keeler in a footnote to Rydberg's paper point out that there occurs in the spectra of several nebulæ a line at

$\lambda = 4687$. Finally, there are given in Table X. more accurate measurements of the wave-lengths of the lines of the Pickering series together with the values calculated by Rydberg's formula for the sharp series of hydrogen.

TABLE X.

Obse-ved. λ	m	Calculated. λ
5413·6	3	5412·8
4542·4	4	4543·3
4200·7	5	4201·5
4026·0	6	4027·3
3924·0	7	3925·2
3860·8	8	3859·8
3815·7	9	3815·2
3783·4	10	3783·4

Although, as the result of Bohr's theory of spectra and Fowler's experimental verification, we now know that both the Pickering series and the associated principal series have their origin in ionised helium and not in hydrogen, this does not detract from the value of Rydberg's deduction, the essential importance of which lies in the discovery of the principal series.

Indeed, I think it is only right to lay considerable stress on the remarkable nature of Rydberg's work. It was pioneer work of outstanding merit, for it must not be forgotten that when his main work was done the accuracy of measurement of spectral lines was very much below the present-day standard. In spite of this he was able to formulate three very definite conclusions which have since been proved to have a sound theoretical basis. The first of these is that the wave-numbers of all the lines in any spectral series can be represented by the difference between two terms. The second conclusion is that each of these terms contains a constant which is the same for all elements and all series. It is now believed, however, that this number, whilst being constant for all the series in the arc spectra of any one element, is not exactly the same for all elements. Lastly, we have the Rydberg-Schuster law which is now known to be an exact relation. As will be shown later his expression of the Balmer series of hydrogen lines by the equation

$$n = \frac{N}{2^2} - \frac{N}{m^2}, \quad \text{where } m = 3, 4, 5, \text{ etc.},$$

is of fundamental importance.

As our knowledge advances, and there are few fields in which the advance has been so rapid as that of spectral series, we are perhaps in danger of minimising the value of early pioneer work. It might be urged that the Rydberg general formula is not sufficiently accurate for modern use and that better results are obtained by the Ritz or Hicks formulæ which will be discussed below. Rydberg himself only considered his formula to be an approximation to the truth, but even now in the selection of the lines which are associated together in series

this formula is more convenient than any other in the preliminary part of the work (see p. 304).

The Work of Kayser and Runge.—As was stated on p. 4, Runge in 1888 announced that he had noted the existence of lines in spectra, the wave-numbers of which could be expressed by formulæ of the type

$$n = A + B/m + C/m^2$$

or

$$n = A + B/m^2 + C/m^4.$$

The application of this formula to spectral series was studied by Kayser and Runge, and their results were published during the years 1890 to 1893. They found that the best agreement was usually found by using the second of the two formulæ above, but that in certain cases an improvement was obtained by the use of the formula

$$n = A + B/m^2 + C/m^3.$$

It must be remembered that these formulæ represent only the first terms of a converging series, and that the terms containing higher powers of m are omitted. This omission is of little importance when m is large, that is to say, for the smaller wave-lengths, but the results given by the formula do not agree well with those observed when m is small. Kayser and Runge attributed this to the want of terms with higher powers of m, *e.g.* D/m^6.

This formula was criticised by Rydberg as being only an interpolation formula which aims at expressing the wave-numbers of lines in a series with the greatest possible accuracy. Kayser,[1] however, maintained that the formula is not an interpolation formula in the true sense of the word, since ordinary interpolation formulæ do not express the results so well.

Kayser and Runge, recognising that the general standard of spectroscopic work was not sufficiently great to justify accurate calculation of series formulæ, undertook the measurement of wave-lengths of spectral lines to a much closer degree of approximation. They also were the first to reduce the values measured in air to the true values measured in vacuo so as to ensure as great an accuracy as possible. In order to do this they themselves determined the refractive indices of air and their values were universally used until recently, when still better values were published by Meggers and Peters in 1918 (see Vol. I., p. 127).

It may be noted that Kayser and Runge gave names to the series which were different from those used by Rydberg. The nebulous and sharp series were called by the former authors the first and second subordinate series, respectively, and these names are still used by some observers. The more usual names are the diffuse and sharp series. In Table XI. are given the wave-lengths of the series lines of sodium as measured by Kayser and Runge, together with the values

[1] *Handbuch der Spectroscopie*, II., 526.

TABLE XI.

Arc Spectrum of Sodium.

λ.	$\frac{1}{\lambda}$.	Intensity.	Kayser and Runge.						Rydberg.					
			Principal series.		First subordinate series.		Second subordinate series.		Principal series.		Nebulous series.		Sharp series.	
			m		*m*		*m*		*m*		*m*		*m*	
8194·76	12202·92	—		—	3	8194·76*		—		—	2	8203·10		—
8184·33	12218·47	—		—	3	8184·33*		—		—	2	8191·51		—
6161·15	16230·74	8*d*R		—		—	4	6161·15*		—		—	3	6158·66
6154·62	16247·96	8*d*R		—		—	4	6154·62*		—		—	3	6152·15
5896·16	16960·19	9*r*	3	5818·7		—		—	1	5894·39		—		—
5890·19	16977·38	10*r*	3	5804·6		—		—	1	5888·42		—		—
5688·26	17580·07	8*d*R		—	4	5688·26*		—		—	3	5689·70		—
5682·90	17596·65	7*d*R		—	4	5682·90*		—		—	3	5684·14		—
5675·92	17618·29	3*d*V		—		—		—		—		—		—
5670·40	17635·44	3*d*V		—		—		—		—		—		—
5153·72	19403·46	6*d*		—		—	5	5153·72*		—		—	4	5155·30
5149·19	19420·53	5*d*		—		—	5	5149·19*		—		—	4	5150·73
4983·53	20066·10	6*d*R		—	5	4983·53*		—		—	4	4984·36		—
4979·30	20083·14	5*d*R		—	5	4979·30*		—		—	4	4980·09		—
4752·19	21042·93	4*d*		—		—	6	4752·19*		—		—	5	4754·15
4748·36	21059·90	3*d*		—		—	6	4748·36*		—		—	5	4750·26
4669·4	21416·03	4*d*R		—	6	4668·45		—		—	5	4670·31		—
4665·2	21435·31	3*d*R		—	6	4664·68		—		—	5	4666·56		—
4546·03	21997·21	3*d*		—		—	7	4544·86		—		—	6	4547·54
4542·75	22013·10	2*d*		—		—	7	4541·36		—		—	6	4543·88
4500·0	22222·22	2*d*		—	7	4497·32		—		—	6	4499·55		—
4494·3	22250·41	2*d*		—	7	4493·80		—		—	6	4496·07		—
4423·7	22605·51	—		—		—	8	4421·95		—		—	7	4425·56
4420·2	22623·41	—		—		—	8	4418·65		—		—	7	4422·20
4393·7	22759·86	—		—	8	4392·83		—		—	7	4395·31		—
4390·7	22775·41	—		—	8	4389·40		—		—	7	4391·99		—
4343·7	23021·85	—		—		—	9	4342·44		—		—	9	4347·02
													9	4343·77
4325·7	23117·65	—		—	9	4323·94		—		—	7	4326·64		—
											7	4323·42		—
3303·07	30274·87	8*r*	4	3303·07*		—		—	2	3315·73		—		—
3302·47	30280·37	8*r*	4	3302·47*		—		—	2	3315·15		—		—
2852·91	35051·93	6*r*	5	2852·91*		—		—	3	2858·79		—		—
									3	2858·60		—		—
2680·46	37307·03	4*r*	6	2680·46*		—		—	4	2683·64		—		—
									4	2683·55		—		—
2593·98	38550·80	2*r*	7	2593·95		—		—	5	2596·00		—		—
				2593·89		—		—	5	2595·95		—		—
2543·85	39310·49	1*r*	8	2543·75		—		—	6	2545·38		—		—
				2543·61		—		—	6	2545·35		—		—
2512·23	39805·27	1*r*	9	2511·77		—		—	7	2513·34		—		—
				2511·58		—		—	7	2513·33		—		—

* The lines thus marked were used in the calculation of the constants of the formula.

calculated by them. For comparison I have included the results obtained by Rydberg's formula, adopting the values of the constants given by him.

Kayser and Runge's equations are :—

Principal series, (1) $n = 41542{\cdot}51 - 130233/m^2 - 800791/m^4$,
(2) $n = 41550{\cdot}33 - 130710/m^2 - 793751/m^4$.
1st subord. ,, (1) $n = 24492{\cdot}32 - 110585/m^2 - 176{\cdot}6/m^4$,
(2) $n = 24510{\cdot}21 - 110606/m^2 - 177{\cdot}6/m^4$.
2nd subord. ,, (1) $n = 24549{\cdot}12 - 120726/m^2 - 197891/m^4$,
(2) $n = 24565{\cdot}83 - 120715/m^2 - 197935/m^4$.

In Rydberg's equations we have the following constants :—

$$N = 109675{\cdot}00.$$

Principal series, P_∞ or convergence limit 41452·61,

(1) line of larger wave-number $\mu = 1{\cdot}117072$.
(2) line of smaller wave-number $\mu = 1{\cdot}116329$,

Nebulous series, $d = 0{\cdot}649840$,

(1) $D_{1\infty}$ or convergence limit 24470·13,
(2) $D_{2\infty}$,, ,, ,, 24487·32.

Sharp series, $\sigma = 0{\cdot}988436$,

(1) $S_{1\infty}$ or convergence limit 24470·13,
(2) $S_{2\infty}$,, ,, ,, 24487·32.

It may be seen that Kayser and Runge's formula is very successful in reproducing the observed values, except when m is small. Indeed, the agreement between calculation and observation is better than in the case of Rydberg's formula.

On the other hand, the Kayser and Runge formula does nothing more than express the wave-numbers of the lines of a series with accuracy. The fundamental facts of Rydberg's theory are not expressed, and since we know that these have a real physical significance, there is no question that the Kayser and Runge formula has no real advantage except that it is very convenient to use.

This criticism of their formula must in no way be allowed to detract from the value of Kayser and Runge's work on spectral series, for we owe to them a very full knowledge of the series systems characteristic of many elements. It was they who were able to identify and classify the satellite series which are often associated with doublet and with triplet series. The satellite series were first recognised by Rydberg and called by him the secondary nebulous series as explained above on p. 16. Runge and Paschen also carried out very valuable work on the spectral series of helium,[1] oxygen, sulphur, and selenium.[2] Particular reference may be made to the case of helium, for this

[1] *Berl. Ber.*, 639 (1895) ; *Brit. Ass. Report*, 610 (1895).
[2] *Ann. der Phys.*, **61**, 641 (1897) ; *Astrophys. Journ.*, **8**, 70 (1898).

element exhibits six series, of which two are principal series, two first subordinate, and two second subordinate series. In this case the formula containing the term m^{-3} was more suitable and the values of the constants in the six equations were as follows :—

Principal series,	(1)	$n = 38455{\cdot}324 - 109891/m^2 - 14507/m^3.$
1st subord. ,,	(1)	$n = 29224{\cdot}35 - 109836{\cdot}3/m^2 - 167/m^3.$
2nd ,, ,,	(1)	$n = 29197{\cdot}97 - 106152{\cdot}4/m^2 - 86560/m^3.$
Principal series,	(2)	$n = 32029{\cdot}86 - 109537/m^2 - 1963{\cdot}6/m^3.$
1st subord. ,,	(2)	$n = 27175{\cdot}16 - 109758{\cdot}6/m^2 - 272{\cdot}6/m^3.$
2nd ,, ,,	(2)	$n = 27168{\cdot}595 - 108825{\cdot}6/m^2 - 35960/m^3.$

It will be seen that the first and second subordinate series form two pairs with the same convergence limits, and as there are two principal series Runge and Paschen concluded that helium must be a mixture of two gases, to which, following Johnstone Stoney's suggestion, they gave the names of helium and parhelium. This conclusion, however, was proved to be erroneous.

The Work of Ritz.—Very important and valuable work on spectral series has been carried out by Ritz, who in his earlier papers dealt with the theory of spectral series and the development of a new formula.[1] He starts with Rydberg's equations for the two series of hydrogen lines,

$$n = \frac{N}{m_1^2} - \frac{N}{m_2^2}$$

and

$$n = \frac{N}{m_1^2} - \frac{N}{(m_2 + 0{\cdot}5)^2}$$

and arrives at the general equation for all series

$$n = \frac{N}{p^2} - \frac{N}{q^2}$$

where p and q are the roots of certain transcendental equations. These terms can be expressed in semi-convergent series of the form

$$p = m_1 + \alpha + \frac{\beta}{m_1^2} + \frac{\gamma}{m_1^4} + \ldots$$

$$q = m_2 + \alpha' + \frac{\beta'}{m_2^2} + \frac{\gamma'}{m_2^4} + \ldots$$

It is clear from this that the term N is the same for all substances, as was maintained by Rydberg.

If only the first two terms of the converging series are used we obtain Rydberg's general formula,

$$n = \frac{N}{(m_1 + \alpha)^2} - \frac{N}{(m_2 + \alpha')^2}$$

[1] *Ann. der Phys.*, **12**, 264 (1903); *Phys. Zeitsch.*, **4**, 406 (1903).

which is now shown to be only a first approximation. In order to obtain a second and closer approximation we must take in a third term of the converging series, and not alter the constant N. We thus have for a single series (m_1 = constant)—

$$\pm n = A - \frac{109765{\cdot}00}{\left(m_2 + \alpha' + \frac{\beta'}{m_2^2}\right)^2},$$

where $m_2 = 1, 2, 3$, etc. This formula gives very striking results when applied to spectra. Further, the connection between the principal and second subordinate or sharp series is in this way mathematically proved, and the two can be united in one formula. The doublets of these two series in the spectra of the alkali metals are given by the formulæ

$$\pm n = N\left\{\frac{1}{\left(m_1 + \alpha_1 + \frac{\beta}{m_1^2}\right)^2} - \frac{1}{\left(m_2 + 0{\cdot}5 + \alpha' + \frac{\beta'}{(m_2 + 0{\cdot}5)^2}\right)^2}\right\}$$

$$\pm n = N\left\{\frac{1}{\left(m_1 + \alpha_2 + \frac{\beta}{m_1^2}\right)^2} - \frac{1}{\left(m_2 + 0{\cdot}5 + \alpha' + \frac{\beta'}{(m_2 + 0{\cdot}5)^2}\right)^2}\right\}$$

In the case of sodium and potassium Ritz has calculated out the wave-lengths of the lines, and it will be seen how great an accuracy the formula gives. The values of the constants were

Sodium.	Potassium.
$\alpha_1 = 0{\cdot}14595$, $\alpha_2 = 0{\cdot}14521$, $\beta = -0{\cdot}1158$	$\alpha_1 = 0{\cdot}29034$, $\alpha_2 = 0{\cdot}28750$, $\beta = -0{\cdot}2239$
$\alpha' = 0{\cdot}15157$ $\beta^1 = -0{\cdot}05586$	$\alpha' = 0{\cdot}31789$ $\beta' = -0{\cdot}1076$

In the Tables XII. and XIII. the calculated wave-lengths are not given, but only the differences between these and the observed values. The latter are given in the first column; in the second are given the differences obtained by Kayser and Runge, the asterisks meaning that the observed values were used to obtain the constants in the formula. In the third column are given the differences obtained by Ritz.

TABLE XII.

Sodium.

Principal Series.

m_1		KR	R	m_1		KR	R
2	5896·16	+ 78	0·00	6	2593·08	+ 0·03	− 0·13
	5890·19	+ 86	0·00			+ 0·09	0·08
3	3303·07	00*	+ 0·03	7	2543·85	+ 0·10	− 0·22
	3302·47	00*	00			+ 0·24	− 0·19
4	2852·91	00*	− 0·10 + 0·07	8	2512·23	+ 0·5	− 0·15
						+ 0·6	− 0·12
5	2680·46	00*	− 0·08 0·00				

Second Subordinate Series.

$m_2 + \frac{1}{2}$		KR	R
1·5	5890·19	+ 334·0	0·00
2·5	11404·0	− 1·14	+ 0·9
3·5	6161·15	− 0·00*	0·00
4·5	5153·72	0·00*	− 0·25
5·5	4752·19	0·00*	− 0·23
6·5	4546·03	+ 1·16	+ 0·21
7·5	4423·7	+ 1·7	− 0·17

Only one line of the pairs is given in this series, as they have a constant frequency difference.

TABLE XIII.

POTASSIUM.

Principal Series.

m_1		KR	R	m_1		KR	R
2	7701·92	+ 161·3	0·00	7	3034·94	+ 0·23	− 0·20
	7668·54	+ 150·6	− 0·24		3034·94	+ 0·44	− 0·05
3	4047·36	0·00*	0·00	8	2992·33	+ 0·68	− 0·19
	4044·29	0·00*	0·00			+ 0·80	− 0·08
4	3447·49	0·00*	+ 0·13	9	2963·36	+ 1·05	− 0·13
	3446·49	0·00*	+ 0·12			+ 1·11	− 0·07
5	3217·76	0·00*	0·00	10	2942·8	+ 1·45	− 0·27
	3217·27	0·00*	+ 0·05			+ 1·60	− 2·23
6	3102·37	+ 0·27	+ 0·10				
	3102·15	+ 0·36	+ 0·40				

The second subordinate series of potassium agrees with the observed values just as closely as in the case of sodium. This formula, developed by Ritz, marked a great advance in our knowledge of spectral series, since it established the truth of the contentions made by Rydberg, namely, the constancy of the term N, the expression of the wave-number of the lines of any series as the difference between two terms, one constant and the other variable, and the connection between the various series exhibited by one element. The Ritz equation,

$$n = \mathrm{A} - \frac{\mathrm{N}}{\left[m + \alpha + \frac{\beta}{m^2}\right]^2},$$

has been adopted by many as the most accurate formula for the expression of the lines of a spectral series.

In later papers Ritz [1] showed how it is possible from the more accurate values given by his formula to derive new series of lines from the known spectral series of an element. He brought forward a modified formula

$$n = \mathrm{A} - \frac{\mathrm{N}}{[m + \alpha + \beta(\mathrm{A} - n)]^2}$$

[1] *Astrophys. Journ.*, **28**, 237 (1908); *Phys. Zeit.*, **9**, 244, 521 (1908).

and it is of some importance to note that in his later work Ritz relied upon this formula as the more accurate of the two. The constants α and β characterise the course of the series and are equal to one another for two series that have constant differences.

The new advance made by Ritz in the establishment of new series is a generalisation of fundamental importance and is known as the combination principle. The possibility of such series had occurred to Rydberg, but he was unable to prove their existence. This may readily be understood if we take Rydberg's formula—

$$n = \frac{N}{(m_1 + \mu_1)^2} - \frac{N}{(m_2 + \mu_2)^2},$$

which for the principal series takes the form

$$n = \frac{N}{(1 + \sigma)^2} - \frac{N}{(m_2 + \mu_2)^2},$$

where σ is the value of μ in the sharp series. It occurred to Rydberg that in his general formula m_1 might vary as well as m_2, and that lines might exist, the wave-numbers of which, for instance, are given by

$$n = \frac{N}{(2 + \sigma)^2} - \frac{N}{(m_2 + \mu_2)^2}.$$

As I say, Rydberg was not able to identify any such lines, but Ritz definitely established the new principle, for he discovered the existence of these combination lines and series of lines. A typical and very simple instance is afforded by hydrogen, the Balmer series of which is represented by the simplified Rydberg formula

$$n = \frac{N}{m_1^2} - \frac{N}{m_2^2}.$$

Ritz showed that if $m_1 = 3$ and $m_2 = 4$ a line is obtained with $\lambda = 18751{\cdot}7$, which is obviously the line measured by Paschen at $\lambda = 18751$. Another line ($m_2 = 5$) of this series has also been recognised. Again, if $m_1 = 1$ and $m_2 = 2, 3, 4$, the very short wave-length lines measured by Lyman are obtained.

Ritz introduced a simplification in the method of expressing the equations of spectral series by writing the symbol (m, α, β) for the variable term $N/[m + \alpha + \beta(A - n)]^2$ which enables us to express the principle of combination very simply. Thus the doublet principal series of the alkali metals may be written in the form

$$n = (2{\cdot}5, s, \sigma) - (m, p_1, \pi_1),$$

and

$$n = (2{\cdot}5, s, \sigma) - (m, p_2, \pi_2),$$

if for α and β we substitute s and σ for the sharp series and p and π for the principal series. Similarly the sharp series is written

$$n = (2, p_1, \pi_1) - (m, s, \sigma)$$

and

$$n = (2, p_2, \pi_2) - (m, s, \sigma),$$

and the diffuse series by

$$n = (2, p_1, \pi_1) - (m, d, \delta)$$
and $$n = (2, p_2, \pi_2) - (m, d, \delta).$$

Combination series have been observed of the types given by putting 3·5, 4·5, etc., in the first term of the equation for the principal series, for example

$$n = (3{\cdot}5, s, \sigma) - (m, p_1, \pi_1).$$

Similarly, new combinations have been observed of the type

$$n = (2, p_1, \pi_1) - (m, p_1, \pi_1)$$
and $$n = (2, p_2, \pi_2) - (m, p_2, \pi_2).$$

It may be readily seen that as combination terms exist in which the variable terms of the satellite series take part, the number of possible combinations is very great. One particular combination noted by Ritz may be mentioned, namely, $(3, d, \delta) - (m, p_1 - p_2, \pi_1 - \pi_2)$ where $m = 4, 5, 6$, etc., which expresses the infra-red series of lines found by Bergmann [1] in the spectra of the alkali metals. This series is now generally recognised as one of the four chief series of a system and is called the fundamental series, a name suggested by Hicks,[2] although it is sometimes still referred to as the Bergmann series. It is expressed on the Ritz method by $(3, d, \delta) - (m, f, \phi)$, where f and ϕ are the characteristic constants. They are not exactly equal, as Ritz believed, to $p_1 - p_2$ and $\pi_1 - \pi_2$.

The great importance of the combination principle may at once be realised from the fact that the combination lines are obtained without the introduction of any new constants. Further, the new principle still further emphasises the fundamental significance of the expression of the wave-number of any line as the difference between two terms. It is this fact which forms the basis of the Bohr theory of elementary spectra, according to which the two terms represent two different energy states of the atom, the radiation corresponding to a spectrum line being emitted when the atom passes from the higher energy state to the lower.[3]

The Series Architecture of Simple Systems.—The foregoing account of the work of Rydberg, Kayser and Runge, Runge and Paschen, and Ritz, brings us to the point when it is advisable to give a short description of the present state of our knowledge of simple series systems, such as we have been discussing. At the moment this can only be done purely as a matter of series structure. It may be said at the outset that the advent of the Bohr theory has very considerably altered our point of view. There is no longer any great need to enter into argument as to the relative merits of any one series formula from the point of view of its physical significance. It is now rather a question

[1] *Zeitsch. wiss. Phot.*, **6**, 113, 145 (1908).
[2] *Analysis of Spectra*, p. 29. Cambridge University Press, 1922.
[3] For an account of Bohr's theory and its developments, see below, p. 63.

of choosing a formula which expresses the wave-numbers of the lines with sufficient accuracy and which at the same time is convenient to use as regards the avoidance of unnecessary complexity of calculation. There is no formula for the spectral series of elements, except those of hydrogen and helium, which has an absolute physical basis on the Bohr conception. All that we know definitely is that the variable term in the formula for any such series is a function of a consecutive series of integers, and that this function is not constant but approaches a constant limiting value as the integers become larger. This is inherent, of course, in Rydberg's formula and in both forms of the Ritz equation and is also characteristic of another formula which may be mentioned here, namely that of Hicks,[1]

$$n = \mathrm{A} - \frac{\mathrm{N}}{\left(m + \alpha + \frac{\beta}{m}\right)^2}$$

Several other formulæ have from time to time been suggested by Halm,[2] Paulson,[3] Johansen,[4] and Ishiwara,[5] and in some cases these give closer agreement with observation than the Ritz and Hicks formulæ are capable of giving. It would seem, however, that at the present state of our knowledge it is hardly worth while to do more than give this brief reference to them.

The first question that arises is which is the best formula to adopt in ordinary work. It may be said that in the preliminary selection of the series lines out of a spectrum the Rydberg formula is very useful, in spite of the fact that it is the least accurate. It is a simple formula to use and with the help of the interpolation table given on p. 300 very valuable information can be gained in the early stages of allocating lines to their series. For the more accurate expression of the lines of a given series, either the Ritz or Hicks formula can be used and indeed the former is used by Paschen and his co-workers, whilst in England Fowler employs the latter.

As regards the complete series system of an element we have already learned that there are four chief series, namely, the principal, diffuse, sharp, and fundamental groups. These consist of either singlets, doublets, or triplets and it is interesting to note that doublet and triplet series are exhibited alternately by the elements in the consecutive groups of the periodic table. Thus the elements of the first group, lithium, sodium, potassium, etc., exhibit doublets, the elements of the second group, magnesium, calcium, etc., exhibit singlets and triplets, whilst in the third group, so far as we have yet learned, aluminium, gallium, etc., doublets again are the characteristic type. This only refers to the arc spectra of the elements, the spark or

[1] For an account of Hicks' work, see below, p. 40.
[2] *Trans. Roy. Soc.*, Edin., **41**, 551 (1905).
[3] *Kongl. Fysiog. Sallsk. Handlingar*, **25**, No. 12 (1914).
[4] *Arkiv. Mat. Ast. och Fysik*, **12**, No. 6 (1917).
[5] *Math. Phys. Soc.*, Tokyo, **9**, 20 (1916).

enhanced spectra showing different types as will be explained below. Reference has already been made to the Ritz abbreviated method of expressing series and this has generally been adopted, but this method refers particularly to Ritz's own equation. A more general system is indicated which does not commit us to any definite formula and Fowler's method may be used. According to this system any variable term is written in general as $m\mu$, or mP, mS, mD, mF for the four chief series. Further, the wave numbers of the mth lines of the four chief series are expressed by P(m), S(m), D(m), F(m). The general equations of the four series are written

$$\begin{aligned} \mathrm{P}(m) &= 1\mathrm{S} - m\mathrm{P}, \text{ principal series.} \\ \mathrm{S}(m) &= 1\mathrm{P} - m\mathrm{S}, \text{ sharp series.} \\ \mathrm{D}(m) &= 1\mathrm{P} - m\mathrm{D}, \text{ diffuse series.} \\ \mathrm{F}(m) &= 2\mathrm{D} - m\mathrm{F}, \text{ fundamental series.} \end{aligned}$$

The Rydberg-Schuster law is expressed in the first three, whilst the last, foreshadowed by Ritz, is generally known as Runge's law.[1] The limit of the fundamental series, F_∞, is equal to 2D and from the third equation we have $\mathrm{D}(2) = \mathrm{D}_\infty - 2\mathrm{D} = \mathrm{D}_\infty - \mathrm{F}_\infty$. Runge's law, therefore, can be expressed by saying that the difference between the limits of the diffuse and fundamental series is equal to the wave-number of the first line of the diffuse series (usually with $m = 2$ in Rydberg's formula).

The above method leads to a general statement of the relations between the four series and does not indicate whether the series consists of singlets, doublets, or triplets. Following a suggestion made by Saunders, Fowler [2] uses capital letters for singlet series, small letters for triplet series, and Greek letters for doublet series, thus :—

P, S, D, F, for singlet series,
π, σ, δ, ϕ, ,, doublet ,,
p, s, d, f, ,, triplet ,,

If the complication due to the presence of satellites be for the moment omitted we may describe the characteristics of doublet and triplet series. The principal series of doublets consists of pairs, the components of which approach one another as the order number (m) increases and the convergence frequency is the same for both series of components. The more refrangible components of the pairs are the stronger lines and the wave-number difference of the first pair ($m = 1$) is the same as that for the pairs of the sharp and diffuse series.

The sharp and diffuse series consist of pairs of constant wave-number difference, and, in accordance with the Rydberg-Schuster law, the less refrangible components of the lines are the stronger. On the abbreviated system of notation these facts may be expressed in the following way :—

[1] *Phys. Zeit.*, **9**, 1 (1908).
[2] *Report on Series in Line Spectra.* Fleetway Press, London, 1922.

Principal series $\begin{cases} \pi_1(m) = 1\sigma - m\pi_1, \text{ shorter } \lambda \text{ and stronger intensity,} \\ \pi_2(m) = 1\sigma - m\pi_2, \text{ longer } \lambda \text{ and weaker intensity,} \end{cases}$
$m = 1, 2, 3, \text{ etc.}$

Sharp series $\begin{cases} \sigma_1(m) = 1\pi_1 - m\sigma, \text{ longer } \lambda \text{ and stronger intensity,} \\ \sigma_2(m) = 1\pi_2 - m\sigma, \text{ shorter } \lambda \text{ and weaker intensity,} \end{cases}$
$m = 2, 3, 4, \text{ etc.}$

Diffuse series $\begin{cases} \delta_1(m) = 1\pi_1 - m\delta, \text{ longer } \lambda \text{ and stronger intensity,} \\ \delta_2(m) = 1\pi_2 - m\delta, \text{ shorter } \lambda \text{ and weaker intensity,} \end{cases}$
$m = 2, 3, 4, \text{ etc.}$

As regards the fundamental series the general equation given above is $F(m) = 2D - mF_1$, and since it will be seen from the above expressions that there is only one value of the term 2δ, it follows that the fundamental series consists of single lines. In order to be in keeping with the symbols employed for a doublet series, this series is written

$$\phi(m) = 2\delta - m\phi$$
$$m = 3, 4, 5, \text{ etc.}$$

It is clear that the constant separation of the components of the sharp and diffuse series and that of the first pair of the principal series is given by $1\pi_2 - 1\pi_1$.

In a triplet series the least refrangible components of the sharp and diffuse triplets have usually the strongest intensities, that of the most refrangible components being the weakest. If the wave-numbers in decreasing order of wave-length be called n_1, n_2, n_3, then $n_2 - n_1$ is usually rather more than $2(n_3 - n_2)$.

In the principal series the order of intensities is inverted and the two most refrangible components have the widest separation, except, as is usually true, in the case of the first member of the series. In this series, as is true of all principal series (except singlets), the component series have the same convergence limit ($1s$). For the same reason, as given above, the fundamental series consists of singlets. In the abbreviated notation the various equations are written

Principal series $\begin{cases} p_1(m) = 1s - mp_1, \text{ shortest } \lambda \text{ and strongest intensity,} \\ p_2(m) = 1s - mp_2, \\ p_3(m) = 1s - mp_3, \text{ longest } \lambda \text{ and weakest intensity,} \end{cases}$
$m = 1, 2, 3, \text{ etc.}$

Sharp series $\begin{cases} s_1(m) = 1p_1 - ms, \text{ longest } \lambda \text{ and strongest intensity,} \\ s_2(m) = 1p_2 - ms, \\ s_3(m) = 1p_3 - ms, \text{ shortest } \lambda \text{ and weakest intensity,} \end{cases}$
$m = 2, 3, 4, \text{ etc.}$

Diffuse series $\begin{cases} d_1(m) = 1p_1 - md, \text{ longest } \lambda \text{ and strongest intensity,} \\ d_2(m) = 1p_2 - md, \\ d_3(m) = 1p_3 - md, \text{ shortest } \lambda \text{ and weakest intensity,} \end{cases}$
$m = 2, 3, 4, \text{ etc.}$

Fundamental series $f(m) = 2d - mf,$
$m = 3, 4, 5, \text{ etc.}$

In the case of the fundamental series the convergence limit $2d$ is always the first variable term of the diffuse series and is sometimes given by $m = 1$ and at most times by $m = 2$.

In the case of the elements which show triplet series there is exhibited also a system of singlets, and since in addition to combination lines within each system there also appear inter-combinations between each system, Fowler quite rightly suggested that the singlet system forms an essential feature of a triplet system.

When satellites are present the structure of a series system is more complicated. Mention has already been made of the discovery of satellites by Rydberg who called them secondary nebulous series. Kayser and Runge were the first to point out their real connection with the diffuse series. Both doublet and triplet series have satellites associated with them, although this is not always the case since neither sodium nor magnesium exhibit any evidence of satellites. This, however, is due to the fact that the satellites have not been separated from the principal lines.

In the case of doublet series there is one satellite which is associated with the less refrangible component of each pair of the diffuse series, the satellite in general having a weaker intensity and a larger wave-length. It is a remarkable fact that the chief line is then displaced from its normal position, the constant separation characteristic of the diffuse pairs now being shown by the satellite and the more refrangible component of the pair. As the order number m increases the chief line and its companion satellite approach closer together, the common limit being the same as that of the corresponding members of the sharp series. In short, the less refrangible line and its satellite have the normal convergence limit. Since the satellites are only associated with the diffuse series, the formulæ for the principal and sharp series are the same as given above for doublet series, but the formulæ for diffuse and fundamental series are altered. For the diffuse series we have

$$\delta_1'(m) = 1\pi_1 - m\delta', \text{ satellite,}$$
$$\delta_1(m) = 1\pi_1 - m\delta, \text{ chief component with longer } \lambda,$$
$$\delta_2(m) = 1\pi_2 - m\delta, \quad ,, \quad ,, \quad ,, \text{ shorter } \lambda.$$

For the first time we have now two values for the limit of the fundamental series usually given by $2D_1$, for we have $2\delta'$ and 2δ. In the case of doublet series, therefore, when satellites are present the fundamental series consists of doublets, and these doublets have a constant wave-number difference equal to the separation of the satellite and chief component in the first diffuse pair for which as a rule $m = 2$. We have therefore

$$\phi_1(m) = 2\delta - m\phi, \text{ longer } \lambda, \text{ greater intensity,}$$
$$\phi_2(m) = 2\delta' - m\phi, \text{ shorter } \lambda, \text{ weaker intensity.}$$

In a triplet system each member of the diffuse series has three satellites associated with it, the least refrangible component having

two, the middle component one, and the most refrangible component no satellite. The weakest intensity is shown by the satellite with the larger wave-length associated with the least refrangible chief component of the triplet, that is to say, the outer satellite. The displacement of the chief line noted in the case of the doublets is here also present for both chief lines having satellites. The normal separation, namely, that given by the sharp triplets, is shown between the outer satellite of the least refrangible chief component and the satellite of the middle chief component. Just as in the case of the doublet series, the chief component and its satellite or satellites approach closer together as the order number increases. Each triplet consists therefore of six lines, three chief lines and three satellites, and there

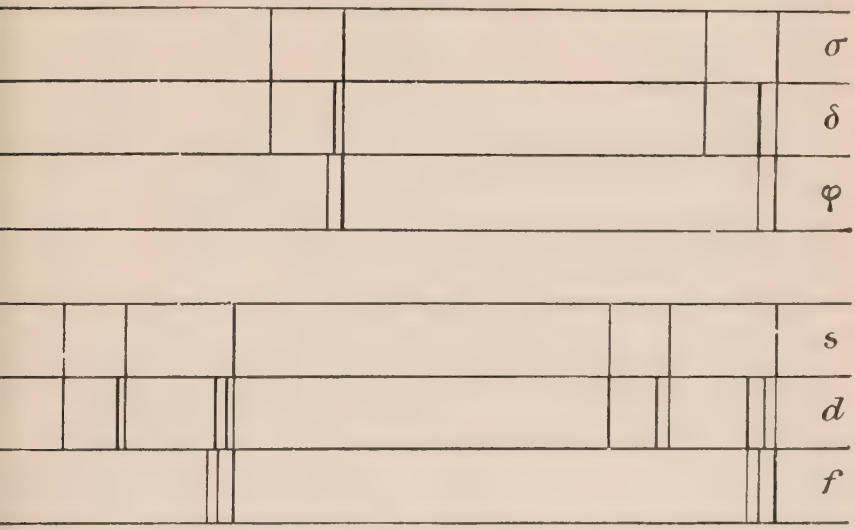

FIG. 1.

(From Fowler's "Report on Series in Line Spectra." Fleetway Press.)

are three convergence limits which are the same as those of the corresponding lines of the sharp series. The series equations are written thus :—

$$d_1''(m) = 1p_1 - md'', \text{ satellite, weakest intensity,}$$
$$d_1'(m) = 1p_1 - md', \text{ satellite,}$$
$$d_1(m) = 1p_1 - md, \text{ chief line with longest } \lambda,$$
$$d_2''(m) = 1p_2 - md'', \text{ satellite,}$$
$$d_2(m) = 1p_2 - md, \text{ middle chief line,}$$
$$d_3''(m) = 1p_3 - md'', \text{ chief line with shortest } \lambda.$$

In this case we have three values for the convergence limit of the fundamental series, namely $2d$, $2d'$, and $2d''$, and consequently the fundamental series will consist of triplets with constant wave-number

differences between the components, which are equal to the wave-number differences between the first chief line and its two satellites in the first triplet of the diffuse series. We thus have for the fundamental series

$$f_1(m) = 2d \quad - mf, \text{ longest } \lambda, \text{ strongest intensity},$$
$$f_2(m) = 2d' \quad - mf,$$
$$f_3(m) = 2d'' - mf, \text{ shortest } \lambda, \text{ weakest intensity}.$$

Diagrammatic arrangements of the chief lines and the satellites are shown in Fig. 1, together with the corresponding structure of the members of the fundamental series.[1]

As an example of a doublet series showing satellites the diffuse pairs of cæsium are given in Table XIV.

TABLE XIV.

	λ.	n.	dn.	Δn.
$m = 2$	36127·0	2767·3 (satellite)	97·9	
	34892·0	2865·2 (first chief line)		554·1
	30100·0	3321·4 (second chief line)		
$m = 3$	9208·40 (1)	10856·7	42·8	
	9172·23 (2)	10899·5		554·0
	8761·35 (5)	11410·7		
$m = 4$	6983·37 (5)	14315·8	20·9	
	6973·17 (10)	14336·7		554·0
	6723·18 (10)	14336·7		
$m = 5$	6217·27 (1)	16079·8	11·4	
	6212·87 (8)	16091·2		553·6
	6010·33 (7)	16633·4		
$m = 6$	5847·64	17096·2	8·6	
	5844·7	17104·8		554·9
	5663·8	17651·1		

In the column headed dn are given the wave-number differences between the satellite and the first chief line and as can be seen these differences decrease as m increases. In the last column the constant difference Δn is that between the satellite and the second chief line, and this is the same as the separation of the pairs of the sharp series and of the first principal pair. The figures in brackets after the wave-lengths are the intensities of the lines.

As an example of triplets showing satellites the members of the diffuse series of mercury are given in Table XV.

[1] Fowler, *loc. cit.*, p. 20.

TABLE XV.

	λ.	n.	dn.	Δn.
$m = 2$	3662·88 (4r)	27293·2 (outer satellite)		
			60·1	
	3654·83 (6)	27353·3 (inner satellite)		
			35·1	
	3650·15 (10)	27388·4 (first chief line)		
				4630·7
	3131·56 (7)	31923·9 (satellite)		
			60·1	
	3125·66 (8)	31984·0 (second chief line)		
				1767·3
	2967·28 (5)	33691·2 (third chief line)		
$m = 3$	3025·52 (2)	33041·6		
			23·5	
	3023·47 (3)	33065·1		
			21·5	
	3021·50 (5)	33086·6		
				4630·9
	2653·68 (4)	37672·5		
			23·3	
	2652·04 (5)	37695·8		
				1767·3
	2534·77 (4)	39439·8		
$m = 4$	2805·42 (1)	35635·0		
			12·1	
	2804·46 (2)	35647·1		
			12·5	
	2803·48 (4)	35659·6		
				4631·6
	2482·72 (3)	40266·6		
			11·5	
	2482·01 (4)	40278·1		
				1767·2
	2378·34 (3)	42033·8		

In the column headed *dn* are given consecutively the wave-number differences between the outer and inner satellite and the first chief line, and between the satellite and second chief line. Under Δn are given for each triplet the characteristic separations which are also shown by the sharp triplets. These separations in the diffuse triplets are given by the outer satellite and the second chief line, and by the satellite to the second chief line and the third chief line.

In addition to this the fundamental series also at times exhibit satellites, the arrangement of these being of exactly the same type as of those accompanying the diffuse terms. The existence of these was first suggested by Hicks [1] and a typical instance is afforded by barium. The first diffuse triplet of barium has the structure shown in Table XVI.

TABLE XVI.

	λ.	n.	dn.	Δn.
$m = 1$	— 22313·4	— 4480·6 (outer satellite)		
			181·6	
	— 23255·3	— 4299·0 (inner satellite)		
			380·8	
	— 25515·7	— 3918·2 (first chief line)		
				878·0
	— 27751·1	— 3602·6 (satellite)		
			181·5	
	— 29233·9	— 3421·1 (second chief line)		
				370·7
	— 30933·8	— 3231·9 (third chief line)		

[1] *Analysis of Spectra*, pp. 54, 134.

Since the fundamental series is derived from this triplet, the three chief lines of the fundamental triplets will have the constant separations of 380·8 and 181·6 respectively. The complete structure of a fundamental triplet of barium is shown in Table XVII.

TABLE XVII.

	λ.	*n*.	*δn*.	Δ*n*.
$m = 3$	3997·92	25006·1 (outer satellite)	14·1	
	3995·66	25020·2 (inner satellite)	14·2	
	3993·40	25034·4 (first chief line)		381·2
	3937·88	25387·3 (satellite)	13·9	
	3935·72	25401·2 (second chief line)		181·5
	3909·92	25568·8 (third chief line)		

Attention must be drawn to the negative wave-numbers which are sometimes given by the series formulæ, for these lead to results which at first sight appear to be out of keeping with the general scheme of the arrangement of lines in series. It has already been shown from the Rydberg-Schuster law that the first member of the sharp series is identical with the first member of the principal series, but that the wave-numbers have opposite signs. Thus in the arc spectrum of sodium the two D lines form the first pair of the principal series and also the first pair of the sharp series. The value of 1σ for sodium is 41449·00 and the values of $1\pi_1$ and $1\pi_2$ are 24475·65 and 24492·83, respectively. For $m = 1$ in the two series we have, therefore,

Principal, 41449·00 − 24475·65 = 16973·35 or $\lambda = 5889{\cdot}963$,
41449·00 − 24492·83 = 16956·17 or $\lambda = 5895{\cdot}930$.

Sharp, 24475·65 − 41449·00 = − 16973·35 or $\lambda = -5889{\cdot}963$.
24492·82 − 41449·00 = − 16956·17 or $\lambda = -5895{\cdot}930$

For the next members of the two series the wave-lengths are

	Principal λ.	Sharp λ.
$m = 2$,	3302·35	11404·2
	3302·94	11382·4
$m = 3$,	2852·828	6160·725
	2853·031	6154·214

The true first member of the sharp series, compared with the other members, is a reversed doublet having smaller wave-lengths than the second and third members. This is the more usual phenomenon. In the case of the group, aluminium, gallium, indium, and thallium, the opposite occurs, for it is the first member of the sharp series of doublets which has the positive values and the first member of the principal series which has the negative values. The wave-lengths of

the first four members of the principal series of aluminium are given in Table XVIII.

TABLE XVIII.

	λ
$m = 1$,	— 3961·540
	— 3944·032
$m = 2$,	13125·36
	13151·65
$m = 3$,	6696·064
	6698·734
$m = 4$,	5557·08
	5557·95

In this case it is the first member of the principal series which seems out of keeping with the rest of the series. The explanation of this phenomenon will be given when the Bohr theory is discussed.

The foregoing represents the usual phenomena observed with the four chief spectral series of the elements, so far as these have been observed. In additon to this there are the lines and series of lines due to the combination principle. As already pointed out the possibilities of these are very numerous and many lines have been identified as being due to single combinations, whilst many others have been allocated to combination series.

In spite of the many lines which fall naturally into the four chief series and their normal satellite attendants, and of the many possibilities which are given by the combination principle, there are few elements for which the whole of the observed lines have been definitely accounted for. A suggestion was made by Hicks that summation lines also occur. In the foregoing, emphasis has been laid throughout on the essential fact that the wave-numbers of spectral lines are given by the differences between two terms, one constant and the other variable. The proposal made by Hicks is to the effect that lines are also given by the sums of these terms and he believes that such summation systems include principal, sharp, diffuse, and fundamental series. Hicks gives in his *Analysis of Spectra* tables which include these summation series and there is no doubt that in this way he has been able to offer an explanation of the origin of many lines which do not fall in with the general scheme indicated above.

At the same time it must be pointed out that such summation series are repugnant to the Bohr theory, which states that the emission of a spectrum line is due to the radiation of a definite quantity of energy when an atom passes from a state of higher energy content to a state of lower energy content, these states being represented by the two terms of a spectral series equation. On the Bohr theory a summation of two of these terms cannot represent a loss of energy to which

a spectral radiation must certainly be due. At the same time Hicks has the advantage in that his summation principle is capable of representing lines which do not fit in with the series architecture such as we have defined. The impossibility of summation series on the Bohr theory shows that Hicks's explanation of his summation lines is purely *ad hoc* and can only be accepted as such. The question therefore remains as to the true explanation of these lines, and it can only be said that our knowledge of spectral series of simple systems is as yet insufficient to explain them.

One is justified in such a conclusion, since, although the great majority of lines can be allocated to either one of the chief series or to combination between these, there are still outstanding certain abnormalities. In the first place, the general rules laid down as to intensities and arrangement of satellites are not always obeyed, and then again there are known to exist series of lines which are not expressed at all well by any of the formulæ of Rydberg, Ritz, or Hicks. Such an abnormal series was noted by Rydberg in the case of magnesium, and other such series have been found in calcium and aluminium. The divergence from the normal seems to consist in the fact that the rate of convergence of the lines is not the same for small and large values for m. Whilst it is true that some success has attended the use of special formulæ in expressing these abnormal series, it is questionable whether much information is thereby gained. It is an acknowledged fact that the Ritz and Hicks formulæ express the great majority of series with considerable accuracy, but that they can only be looked upon as approximations to the real truth. Until the true physical formula has been discovered it would seem wiser to acknowledge the limitations of the approximate formulæ and leave to the future the explanation of the abnormal series.

It may be mentioned here that we have only been considering simple systems such as are exhibited by the elements in the first two groups of the periodic table. Recently, owing to the discovery by Catalan of complex groups of lines in the spectra of manganese, we have learned that singlet, doublet, and triplet systems are by no means all that exist. We shall see later that the statement that the first group of elements are characterised by doublet systems, the elements of the second group by triplets, and the elements of the third group by doublets is misleading. Rydberg was the first to point this out and it is known as Rydberg's law of alternation. The actual state of affairs is more complex since the second group is characterised by singlets and triplets, the third group by doublets and quartets, the fourth by singlets, triplets and quintets, and so on. The structure of these more complex groups will be described later on and it will then be shown that the existence of the satellites in the diffuse and fundamental series of doublets and triplets is part of a general series scheme which is larger than we have as yet been able to envisage.

It must be remembered that the whole of the preceding refers

only to arc spectra and that those spectrum lines, usually known as enhanced lines, do not conform to the series formulæ as given above. By enhanced lines, as explained in Vol. II., Chap. II., p. 132, is meant those lines the relative intensities of which are increased or enhanced when the arc discharge is substituted by the condensed spark discharge. Previous to the enunciation of the Bohr theory these lines were somewhat of a mystery as regards their series relationships, but now it has been found as the result of Fowler's work in this country and of Paschen's later work in Germany that they can all be expressed by the accepted formulæ, provided that the Rydberg constant N is multiplied by 2^2, 3^2, or 4^2, etc. This development of spectral series, based on the Bohr theory of emission spectra, forms one of the most interesting chapters in modern spectroscopy and it affords a confirmation of Bohr's fundamental principles which is extraordinarily convincing. In view of the fact that the story could not be told in its completeness without a knowledge of the elementary principles of the Bohr theory, it will be preferable for the present to postpone all detailed discussion of spark spectra. At the same time it was necessary to mention these enhanced spectra at this stage in order to guard against possible misconception as to the scope of what has gone before.

There is one matter which has not yet received proper attention, namely, the value of the Rydberg constant N. Like all spectroscopic standards this has been modified by the introduction of the modern International Standard of wave-lengths, and it is naturally of great importance to fix a value which may be utilised with confidence in any work in this field. It will be remembered that Rydberg finally adopted the value of 109675·00 (when wave-numbers are used) based on the most recent determinations in his day of the wave-lengths of the Balmer series of hydrogen. Not only has a new fundamental standard of wave-length been introduced, but spectroscopic technique has been greatly improved since the time when Rydberg arrived at this value.

A determination of this constant from an accurate measurement of the first six hydrogen lines was undertaken by Curtis,[1] who obtained the values shown in Table XIX., the last column of which shows the values of N calculated from each line separately.

TABLE XIX.

m.	λ.	Probable error.	n.	N.
3	6562·793	0·0017	15233·216	109679·155
4	4861·326	0·0010	20564·793	109678·896
5	4340·467	0·0006	23032·543	109678·776
6	4101·738	0·0013	24373·055	109678·748
7	3970·075	0·0016	25181·343	109678·738
8	3889·051	0·0011	25705·957	109678·750

[1] *Proc. Roy. Soc.*, A, **90**, 605 (1914); **96**, 147 (1919).

As can be seen the value of N tends to decrease as the order number m increases, which suggests that the Balmer formula is not quite exact. On the other hand, it is known that the hydrogen lines are in reality complex, consisting of two components each of which is in itself complex. This phenomenon will be discussed in detail below and it is only necessary to say here that it is not comparable in any way with the doublets which occur in the alkali metal series. The important point at the moment is that the two principal components are very close together and not of equal intensity, and the separation decreases as m increases. The result is that the measured "optical centre of gravity" cannot conform strictly to the Balmer formula. It is not possible in the present state of our knowledge to give an absolute value of N for hydrogen, but Curtis shows that the most probable value on the International Standard is 109678·3 and this may be adopted for all practical purposes without hesitation. It is hardly necessary to point out that it is not possible to determine N from observations on other elements, since the series formulæ are not sufficiently accurate, and furthermore the Bohr theory shows that N depends on the nature of the element.

The Work of Hicks.—An important critical study of spectral series has been published by Professor W. N. Hicks in a series of five papers.[1] He starts from the position that the Rydberg and the Kayser and Runge formulæ are good enough to indicate the existence of series, but not good enough to reproduce the values for spectral lines within the experimental error of their measurement. In seeking a better formula he naturally took that of Rydberg as the basis, since it has only two constants and leads to the well-known relationships between the various series. In the absence of any definite theory of the origin of spectra it was necessary to make some assumption and test it. Hicks assumes that in Rydberg's equation, $n = A - N/D^2$, where $D = m + \mu$, D is some function of m which can be expanded in a series of which $m + \mu$ is the first term. Since Rydberg's formula becomes more exact as m increases, the function should be expansible in negative powers of m, thus

$$D = m + \mu + \alpha/m + \beta/m^2 \ . \ . \ .$$

where α and β are small.

Ritz in his equation (unknown to Hicks in his early work) puts $D = m + \mu + \beta/m^2$ or $m + \mu + \beta/(m + 0{\cdot}5)^2$, but Hicks obtains more accurate results with his formula. It must be noted, however, that Ritz placed greater reliance on the formula

$$n = A - N/[m + \mu + \alpha(A - n)]^2.$$

This will be further discussed below. The first important result obtained by Hicks is that in his formula it is rarely necessary to go beyond the α/m term, that if α and β terms are both included β is

[1] *Phil. Trans.*, A, **210**, 57 (1911); **212**, 33 (1913); **213**, 323 (1914); **217**, 361 (1918); **220**, 335 (1920).

always a small fraction of α, and that α alone gives better agreement than β alone. Possibly, if Rydberg is right in saying that D is a function of $m + \mu$, the true form is

$$D = m + \mu + \alpha/(m + \mu) + \beta/(m + \mu)^2 \ldots$$

Hicks says that there is some indication that this formula suits certain series, for example Rydberg's magnesium series mentioned above, but too much stress must not be laid on the mere fact that a formula reproduces observations unless these are very exact, or comprise the first members and a considerable number of the others. For example, the formula

$$n = 26617{\cdot}09 - N/[m + 0{\cdot}317620 + 0{\cdot}886213/(m + 0{\cdot}31762)]^2$$

reproduces the magnesium series well, but later Hicks found that the formula

$$n = 26609{\cdot}74 - N/(m + 0{\cdot}345117 + 0{\cdot}723502/m)^2$$

also reproduces the observations within the experimental error of measurement. The results are given in Table XX.

TABLE XX.

m.	λ.	Observational error.	Rydberg.	$\alpha/(m + \mu)$.	α/m.
3	5528·75	0·10	*	*	*
4	4703·33	0·05	*	*	*
5	4352·18	0·05	*	*	*
6	4167·81	0·10	*	− 0·08	+ 0·09
7	4058·45	1·00	− 0·20	− 0·31	+ 0·04
8	3987·08	1·00	+ 0·48	+ 0·39	+ 0·89

* These lines were used in the calculation of the constants.

The values in the fourth column are those obtained by the special formula of Rydberg which he suggested for this particular series of lines, namely,

$$n = A + \alpha/(m + \mu)^2 - \beta/(m + \mu)^4.$$

The last three columns give the errors in wave-lengths in the calculated results and are $\lambda_{calc.} - \lambda_{obs.}$. From the results given in the table Hicks concludes that the magnesium lines do not belong to a new kind of series as thought by Rydberg.

Hicks applies his own formula to the alkali metals, but as his calculations are based on Rowland's scale of wave-lengths they need not be given. In discussing the values of the constants he arrives at interesting results for the principal series (stronger components). In the first place, he finds for sodium, potassium, rubidium, and cæsium that the values of μ − 1 are multiples of a number not far

from 0·074. This suggested some relation with the atomic weight, but no direct relation was obvious. Hicks found, however, that the atomic volumes of these elements can be very nearly expressed by the same multiples of another constant. Then again, since he found that the values of $\alpha(\mu - 1)$ for the four elements are the same, it follows that the values of $\mu + \alpha - 1$ should also be multiples of a constant. The values are collected together in Table XXI.

TABLE XXI.

	μ.	α.	$\mu - 1$.	$\mu + \alpha - 1$.	Atomic volume.
Na .	1·148678	− 0·031776	2 × 0·074339	2 × 0·058451	2 × 11·80
K .	1·296480	− 0·062511	4 × 0·074120	4 × 0·058492	4 × 11·15
Rb .	1·366399	− 0·074554	5 × 0·073280	5 × 0·058369	5 × 11·21
Cs .	1·450967	− 0·090077	6 × 0·075161	6 × 0·060148	6 × 11·76

Hicks suggests that the principal series of sodium, potassium, and rubidium can be represented by the formula

$$n = P_\infty - N/[m + 1 - W(1 - 1/m) + 0{\cdot}074560(1 - 0{\cdot}21521/m)s]^2$$

where W is an atomic weight term having the values 0·000370, 0·001466, 0·006444, respectively, and s stands for the integers 2, 4, 5, given in the above table. The term W is $\Delta/2$, where Δ is the difference between the two denominators which give the doublet series. In order to express the principal series of cæsium a small modification in the formula is necessary.

In the second group of the periodic table there are triplet series and consequently two denominator differences Δ_1 and Δ_2. In the zinc, cadmium and mercury group the same rule holds, if W be taken as Δ_2, which is roughly one-half of Δ_1, but as in the case of cæsium a modification is required in the case of mercury. The following forms for the denominators hold :—

Zn, $m + 1 - W(1 - m^{-1}) + 0{\cdot}290534(1 - 0{\cdot}21558m^{-1})$,
Cd, $m + 1 - W(1 - m^{-1}) + 0{\cdot}359854(1 - 0{\cdot}21537m^{-1})$,
Eu, $m + 1 - W(1 - m^{-1}) + 0{\cdot}309930(1 - 0{\cdot}21246m^{-1})$ *
Hg, $m + 1 - W/4 + 0{\cdot}317077(1 - 0{\cdot}21534m^{-1})$.

* Later measurements show that the constant in the case of europium may quite possibly be 0·215.

In the case of magnesium, calcium, and strontium, the matter is complicated by the presence of the term β/m^2 in the denominator, but Hicks shows that β is a multiple of Δ_2, thus

	Mg	Ca	Sr
β	$20\Delta_2$	$14\Delta_2$	$3\Delta_2$.

The constant 0·215 enters into the denominators if they be written in the following form :—

$$\begin{aligned}
&\text{Mg}, \quad m + 1 - \beta(1 - m^{-1}) + 0{\cdot}382462(1 - 0{\cdot}21533m^{-1}) + \beta m^{-2},\\
&\text{Ca}, \quad m + 1 - \beta(1 - m^{-1}) + 0{\cdot}574797(1 - 0{\cdot}21572m^{-1}) + \beta m^{-2},\\
&\text{Sr}, \quad m + 1 - 2\beta(1 - m^{-1}) + 0{\cdot}676156(1 - 0{\cdot}21404m^{-1}) + \beta m^{-2}.
\end{aligned}$$

Hicks gives the following denominators for aluminium, gallium, indium, and thallium :—

$$\begin{aligned}
&\text{Al}, \quad m + 1 - 50\text{W} + 0{\cdot}294286(1 - 0{\cdot}21526m^{-1}),\\
&\text{Ga}, \quad m + 1 - 10\text{W} + 0{\cdot}359895(1 - 0{\cdot}21483m^{-1}),\\
&\text{In}, \quad m + 1 - 2\text{W} + 0{\cdot}325202(1 - 0{\cdot}21478m^{-1}),\\
&\text{Tl}, \quad m + 1 - \text{W} + 0{\cdot}331405(1 - 0{\cdot}21248m^{-1}),
\end{aligned}$$

where as before $2\text{W} = \Delta$. Thallium does not conform, but, as previously, this might be expected for the member with the highest atomic weight in the group. He considers that these results produce a strong conviction that the number 0·21520 is an essential constant.

Hicks gives evidence that the proportionality with atomic volumes is also exhibited in the elements of the second and third groups. He combines his calculations for the principal series of the alkalies with those for the sharp series of the elements of groups II. and III. in the formula

$$n = \text{A} - \text{N}/[m + 1 - \text{W}(1 - 1/m) + a(1 - k/m)sv]^2,$$

where a and k are constants, not very different from $0{\cdot}002740/(1 - k)$ and 0·21520, respectively ; v is the essential atomic volume of the element (possibly the sphere of activity) and s is an integer.

If $k = 0{\cdot}21520$, $a = 0{\cdot}003490$. The values of s for the elements so far considered are as follows :—

Na 2	Mg 8	Zn 9	Al 8	Ga 8
K 2	Ca 7	Cd 8	Sc ?	In 6
Rb 2	Sr 6	Eu 7 ?	Y ?	?
Cs 2	Ba ? 5 or 6	Hg 6	La ?	Tl 5
	?		Yb ?	
	Ra ? 5 or 6			

It must be pointed out, however, attractive though these results are, that the degree of approximation given by the last general formula leaves a good deal to be desired. This is pointed out by Fowler,[1] who gives a comparison between the values of the denominators calculated from the regular series formulæ and from the Hicks general formula ; these are shown in Table XXII.

[1] *Report on Series in Line Spectra*, p. 52. Fleetway Press, Ltd., London, 1922.

TABLE XXII.

Element.	Series.	Atomic volume.	s.	$\Delta/2$.	Δ_2.	True denominator.	From general formula.
K .	π	44·60	2	0·001466	—	(1) 2·233969	2·244315
						(2) 3·265225	3·277078
Ca .	s	25·5	7	—	0·001368	(1) 2·484198	2·488903
						(2) 3·522799	3·555250
Zn .	s	9·33	9	—	0·003475	(1) 2·227899	2·229991
						(2) 3·257479	3·259785

As may be seen the correspondence is far from perfect and, as Fowler says, after the exhaustive investigation made by Hicks it may be doubted whether it is really possible to deduce such a formula which will be applicable to all elements. At the same time it may be suggested that the want of agreement does not necessarily discount the value of Hicks's generalisation. The atomic volume term is difficult to assess with any degree of confidence, for it depends on the density of the element. The remarkable work of Cohen and his co-workers on the allotropy of the metals at once brings into question the reliability for the present purpose of any one value for the density of a solid element. Until the physical significance of the atomic volume term is definitely determined, the generalisation found by Hicks cannot be dismissed as being of little value because the results given by it do not agree very closely with the observations. It may be that the best method of determining the sphere of activity of the atom is not by calculation of the atomic volume of the solid element, since after all spectral series are functions of the elementary atom in the gaseous state.

In his third paper Hicks further develops his theory of the influence of the atomic weight term. He points out that the doublet and triplet separations are roughly proportional to the square of the atomic weight. In the formulæ these separations arise by certain terms being deducted from the denominators of the typical sequences. For example, in the first group, if

$$P_1(m) = A - N/(m + \mu + \alpha/m)^2 = A - N/D^2,$$

then

$$P_2(m) = A - N/(D - \Delta)^2,$$

with the result that the series consists of converging doublets.

In the sharp and diffuse series

$$S_1(\infty) = D_1(\infty) = N/(D_1)^2 \quad \text{and} \quad S_2(\infty) = D_2(\infty) = N/(D_1 - \Delta)^2.$$

The values of Δ will also be roughly proportional to the square of the atomic weight. We may call these the atomic weight terms and write Δ for doublets, Δ_1 and Δ_2 for triplets, and dn for the actual separations. The values of Δ can be found with great accuracy, especially for elements of large atomic weight.

It has been long known that Δ_1/Δ_2 is always slightly larger than 2. It is natural therefore to consider $\Delta_1 - 2\Delta_2$, expressing both in terms of the square of atomic weight. It is at once seen that these differences in many cases are multiples of the same number, about 360, for example Ca 1, Sr 3, Ba 8, Hg 19, and further that in many cases Δ_1 and Δ_2 are themselves multiples of the same number. Since magnesium and zinc with differences of 450 and 543, respectively, could not be brought into line, this method of attack was at first given up. It was later noted that Δ_1 and Δ_2 are both extremely exact multiples of $\Delta_1 - 2\Delta_2$. In fact $\Delta_1 = 31 \times 543{\cdot}446w^2$ and $\Delta_2 = 15 \times 543{\cdot}476w^2$, where $w =$ A.W./100. This can hardly be due to chance since 543·44 is nearly $3/2 \times 360$ previously found and the 450 of magnesium is about $5/4 \times 360$. In other words, with the rough values used $360 = 4 \times 90$, $450 = 5 \times 90$, and $540 = 6 \times 90$. A systematic investigation of all the available date was then undertaken in order to test the theory whether the Δ of elements with doublet and triplet separations are multiples of a quantity proportional to the square of the atomic weight. This quantity may be written $d = qw^2$. Since Δ is the difference of two decimals with six significant figures it is convenient to tabulate $10^6\Delta$. The method adopted may be shown by taking the triplets of calcium, sharp series, the values of dn_1 and dn_2 being 105·89 and 52·09. The value of $S_1(\infty)$ is 33983·45 and from the numbers 33983·45, 34089·34, and 34141·43 the values of the denominators are found to be 1·796470, 1·793679, and 1·792310, from which Δ_1 is 0·002791 and Δ_2 is 0·001369, and these are tabulated as 2791 and 1369. The atomic weight of calcium is 40·124 and on dividing Δ by $(0{\cdot}40124)^2$ we have

$$\Delta_1 = 17336{\cdot}1 \times w^2 = 48 \times 361{\cdot}169 \times w^2.$$

Hicks gives in each case the permissible margin of error calculated from the known error limit in each measurement, but these need not be given here. In Table XXIII. are given the results of these calculations, which reveal a remarkable constancy in the term qw^2. In the table the second column gives the atomic weights, and in the third column the upper figures are the values of dn and the lower figures the values of $10^6\Delta$. In the case of triplets there are of course two sets of values, one for dn_1 and Δ_1 and the other for dn_2 and Δ_2. The fourth column gives in each case the value of $10^6\Delta/w^2$ and the factors for each, whilst the last column gives the differences between the values of the atomic weight factor and the mean value 361·8. If this atomic weight factor is given as about 90 or 180 the differences in the last column refer to these factors multiplied by 4 or 2. The maximum allowable errors are also given in the last column.

It may be seen at once that the two groups which give doublets agree in giving Δ as multiples of a number close to $361{\cdot}8w^2$. Group II. giving triplets requires in several cases multiples of $90w^2$ or $180w^2$. If it be agreed that 361 is the normal type and for numerical comparison we multiply the 90 by 4 and the 180 by 2, and, further, if the

TABLE XXIII.

Element.	Atomic weight.	dn, $10^6\Delta$.	qw^2.	$361{\cdot}8 +$	
Na .	22·998	17·175	14027·96	0·2	
		743·0	155 × 90·50		0·141
K .	39·097	57·87	19224·86	0·92	
		2939	53 × 362·72		3·22
Rb .	85·448	237·54	17715·86	− 0·40	
		12935	49 × 361·40		0·56
Cs .	132·823	553·80	18449·48	− 0·06	
		32551	51 × 361·74		0·33
Cu .	63·56	248·49	18075·8	0·04	
		7311	50 × 361·84		0·80
Ag .	107·88	920·61	23879·34	0·01	
		27791	66 × 361·81		0·2
Mg .	24·362	40·90	14389·05	0·19	
		854	159 × 90·497		1·00
		19·89	6992·33	1·78	
		415	77 × 90·89		3·12
		$\Delta_1 + \Delta_2 =$	59 × 362·36		
Ca .	40·124	105·89	17336·1	− 0·63	
		2791	48 × 361·169		1·52
		52·09	8503·4	− 0·24	
		1369	47 × 180·923		1·00
		$\Delta_1 + \Delta_2 =$	143 × 180·696		
Sr .	87·66	394·35	15401·16	0·59	
		11835	85 × 181·195		0·72
		186·93	7200·4	− 1·78	
		5533	20 × 360·02		0·585
		$\Delta_1 + \Delta_2 =$	125 × 180·82		
Ba .	137·43	878·21	15528·2	− 0·68	
		29328	43 × 361·121		0·600
		370·33	6340·96	0·54	
		11976	35 × 181·170		0·882
		$\Delta_1 + \Delta_2 =$	121 × 180·74		
Ra .	226·4	2050·26	18077·15	− 0·257	
		92658	50 × 361·543		2 (?)
		832·00(?)	6709·3	0·86	
		34390	37 × 181·33		
		$\Delta_1 + \Delta_2 =$	137 × 180·92		
Zn .	65·40	388·905	16843·68	0·423	
		7204·42	31 × 543·334		0·420
		190·093	8150·74	0·456	
		3486·20	15 × 543·383		0·420
		$\Delta_1 + \Delta_2 =$	46 × 543·356		

TABLE XXIII.—*Continued.*

Element.	Atomic weight.	dn, $10^6\Delta$.	qw^2.	361·8 +	
Cd .	112·3	1170·848	18321·33	− 0·8	
		23105·56	203 × 90·252		0·646
		541·892	8221·64	− 0·408	
		10368·54	91 × 90·348		0·644
		$\Delta_1 + \Delta_2 =$	49 × 541·50		
Eu .	151·93	2630·5	22191·06	− 0·98	
		51223	123 × 180·41		0·68
		1004	7940·57	− 0·94	
		18329	22 × 360·93		0·39
		$\Delta_1 + \Delta_2 =$	333 × 90·485		
Hg .	200·3	4630·648	21888·03	− 0·015	
		87814·99	121 × 180·892		2·12
		1767·01	7478·05	− 1·41	
		30002·3	83 × 90·096		1·15
		$\Delta_1 + \Delta_2 =$	54 × 543·816		
Al .	27·10	112·15	23884	0·079	
		1754	66 × 361·879		1·635
Ga .	69·9	826·10	27715	− 1·87	
		13498	77 × 359·93		3·17
In .	114·8	2212·38	28593·88	− 0·147	
		37684	79 × 361·947		3·32
Tl .	204·04	7792·39	32223·62	0·263	
		134154	89 × 362·063		0·18
Sc .	44·1	320·80	36714	− 0·086	
		7140	203 × 180·857		9·45
		or 6404	91 × 361·89		
He .	3·99	1·007	20860	0·35	
		33·377	58 × 361·45		1
O .	16	3·65	6692	− 0·01	
		171·3	37 × 180·895		5
		2·03	3714·9	1·0	
		95	41 × 90·20		2
		0·62	$14\delta_1$		
		34			
S .	32·07	17·96	10150·85	0·34	
		1044	28 × 362·14		3
		11·21	6329·7	− 0·46	
		651	35 × 180·67		1·5
		$\Delta_1 + \Delta_2 =$	91 × 181·1		
Se .	79·2	103·70	10192	2·20	
		6392	28 × 364·00		3 (?)
		44·69	4363·4	1·81	
		2737	12 × 363·61		3 (?)
		$\Delta_1 + \Delta_2 =$	161 × 90·40		

results are weighted by the estimated limits given in the last column, the method of least squares gives for the value of this constant—

Group I.	361·900
Group II.	361·720
Group III.	362·051
All three groups	361·890 ,

Again, if $d = 361{\cdot}890/4$ the values of Δ for the first of each sub-group may be written—

I.		II.		III.		IV.
Na	Cu	Mg	Zn	Sc	Al	S
$155d$	$50 \times 4d$	$32 \times 5d$ [1]	$31 \times 6d$	$52 \times 7d$	$33 \times 8d$	$8 \times 14d$.

Moreover, the same multiples of d recur in several elements of the same group, for example, $\Delta_1 + \Delta_2$ for zinc, cadmium, and mercury, and europium are all multiples of $6d$, whilst $5d$ occurs in magnesium,[1] strontium, barium, and radium.

The evidence would seem to be conclusive that the atomic weight term is a multiple of a quantity very close to one-quarter of $361{\cdot}8 \times w^2$, and to this quantity Hicks gives the name "oun." Summing up the whole of the evidence, he concludes that the true value of the oun is 90·4725 ± 0·0125.

Hicks proceeds to apply his conception of the oun to the existence of what he calls "collaterals" or lateral displacements by the atomic weight term. Thus the first set in doublet or triplet, sharp or principal series is always the stronger, and the second, or second and third components are considered as having received a displacement by Δ or Δ_1 and Δ_2, and are therefore looked on as collaterals of the first. This displacement is not confined to the generally recognised series, but is of common occurrence and, indeed, depends not only on the Δ but also on other multiples of d. Hicks says that in fact the doublet and triplet series with their satellites are only special cases of a law of very wide application. In general, the wave-number of a line is determined by a formula of the form $N/D_1^2 - N/D_m^2$ and lateral displacements may be produced by the addition (or subtraction) of δ, say xd, or $x\Delta$, to D_1 or D_m. This is indicated by writing xd to the left of the symbol of the original line when it is added to D_1, and to the right when added to D_m. Thus Ca s_1 (2) has $\lambda = 6162{\cdot}46$ and the line with $\lambda = 6439{\cdot}36$ is a collateral represented by $(2\Delta_1 + 10\Delta_2)$ Ca s_1 (2) $(+ \Delta_2)$.

For Ca s_1 (2) $n = N/(1{\cdot}796470)^2 - N/(2{\cdot}484994)^2$,

,, $\lambda = 6439{\cdot}36$, $n = N/(1{\cdot}796470 + 2\Delta_1 + 10\Delta_2)^2 - N/(2{\cdot}484994 + \Delta_2)^2$

$= N/(1{\cdot}815732)^2 - N/(2{\cdot}486362)^2$.

[1] This does not seem to be correct, as in Table XXIII. the factors are given as $159 \times d$.

Hicks shows that this principle can be applied extensively, but it is hardly necessary to give the details, since there must be some doubt as to how far many of his conclusions will be definitely established when sufficiently accurate observations have been made. For the same reason reference only will be made to his extension of the conception of the collaterals. He attempts, with some success it is true, to associate those lines in the spectrum which do not belong to a series with those which form members of the four recognised series. He regards each line of a recognised series as being connected with other lines in the spectrum by several constant wave-number differences or "links." He further believes that these links may be varied in certain definite ways. It is obvious that in a complex spectrum the existence of, say, seven links, coupled with the variations in these, will lead to many accidental coincidences, but Hicks states that the law of probabilities shows that his results are not due to chance.

Mention may also be made of the fact that Hicks claims in his fifth paper to have discovered quite a new type of series. Whereas the recognised series are expressed by the difference of two terms

$$n = \mathrm{A} - \mathrm{N}/(m + \mu + \alpha/m)^2,$$

the new series are expressed by the sum of two terms

$$n = \mathrm{A} + \mathrm{N}/(m + \mu + \alpha/m)^2.$$

He gives a series of this type which he has found in xenon, namely, the summation of the terms of the fundamental series, and says that the existence of these summation series is thoroughly established in other cases.

Reference was made previously on p. 37 to this summation principle of Hicks and the overwhelming evidence against it on the Bohr theory was advanced in favour of its abandonment. It is of some interest now to consider the case of xenon, many of the lines of which Hicks explains by this principle. Although the spectrum of this element has not been elucidated, we know that it belongs to a system which is of an even higher order of complexity than the singlet, doublet, triplet, etc., systems with which we have been dealing. To this more complex type the spectrum of neon belongs and this has been worked out in a most remarkable way by Paschen. As we shall see presently the chief characteristic is a considerable number of series of constant wave-number differences, very closely situated and running parallel to one another. Such a structure can readily be shown to lend itself to some of its lines being expressed by summation of terms, though of course this by no means justifies the use of that principle. I mention this because of the probability that the xenon spectrum is analogous to that of neon, and consequently it would seem that, independently of the Bohr theory, Hicks's summation theory is unnecessary and unjustified.

More recently Hicks [1] has been able to extend his calculations of

[1] *Analysis of Spectra*, p. 124. Cambridge University Press, 1922.

the value of the oun for the elements, owing to the increase in accuracy of the observed values, which has enabled him in many cases to determine the series limits very much more closely. He now presents the evidence for the reality of the oun by adopting a more accurate value of q, tabulating the atomic weights calculated from the spectral measures and contrasting them with the observed chemical values. In the older method, that of comparing the values of q in each individual case, the deduced value of q involved the combined errors due to both spectral and chemical measures. He now keeps the two uncertainties apart and the spectral atomic weights with estimated uncertainties are directly compared with the chemical values and their uncertainties. Since q must ultimately depend on chemical measures it is determined once and for all in the case of silver, for which both the atomic weight and Δ are known with great accuracy, being 107·88 and 27789·10 respectively. We have, therefore,

$$\begin{aligned} 27789{\cdot}10 &= m \times qw^2 \\ &= 66 \times 421{\cdot}0473 \\ &= 66 \times q \times (1{\cdot}0788)^2 \end{aligned}$$

and hence $q = 361{\cdot}78.$

The uncertainty in this value is 0·05 and therefore Hicks adopts $361{\cdot}78 \pm 0{\cdot}05$ as the standard value for q. Expressed as a change in a denominator this is $361{\cdot}78 \times 10^{-6}$ or $361{\cdot}78 \times 10^{-10}$ in terms of the real atomic ratio to hydrogen. If it is dependent on the fundamental atomic constants it must be a function of e^2/hc, and is very near to

$$\frac{4}{3 \times 5}\left(\frac{e^2}{\pi hc}\right)^2.$$

It must be remembered that the oun is one-quarter of qw^2 but, in view of the fact that qw^2 occurs so often, it is more convenient to tabulate all the results in terms of qw^2. For example, the oun of lithium is 0·4455 and $\Delta = 11{\cdot}58 = 26 \times 0{\cdot}4455$ and this is tabulated as $6\frac{1}{2} \times 1{\cdot}782$. In Table XXIV. are given the complete results obtained by Hicks, the second column containing the values of the separations, that is to say ν or ν_1, ν_2 and $\nu_1 + \nu_2$. In the case of triplet series the value of qw^2 is calculated from $\nu_1 + \nu_2$ since Hicks finds that the middle line of a triplet is slightly displaced. In the fifth column are given the values of the atomic weights calculated from qw^2, which are of course given by $100\sqrt{\frac{qw^2}{361{\cdot}78}}$, since as before $w = \text{A.W.}/100$. The numbers given in brackets after the values represent the estimated uncertainties in the last digits of those values. Thus, in the value of Δ for copper 7307·087(150) represents $7307{\cdot}087 \pm 0{\cdot}150$.

TABLE XXIV.

	ν.	Δ.	$m \times qw^2$.	Spectral atomic weight.	Chemical atomic weight.
He	1·007	33·37	58 × 0·5753	3·985	3·99
A	179·50	2519	$43\frac{3}{4}\times$ 57·59		
	75·60	1055·60	$18\frac{1}{4}\times$ 57·91		
	255·10 (100)	3576·89	62 × 57·70 (23)	39·94 (8)	39·88 (?)
Kr	786·45	10969	44 × 249·30		
	309·20	4244	17 × 249·63		
	341·16	4680	$18\frac{3}{4}\times$ 249·63		
	1095·65	15213·56	61 × 249·40 (17)	83·029 (27)	82·92 (?)
	1127·61 (70)	15650·21	$62\frac{3}{4}\times$ 249·40		
X	1777·90	24893·14	$40\frac{3}{4}\times$ 610·87		
	815·05	10996·29	18 × 610·89		
	2592·95	35889·43 (158)	$58\frac{3}{4}\times$ 610·88 (30)	129·94 (3)	130·20 (?)
Nt	5371	72824	$40\frac{3}{4}\times$ 1787·09		
	2649	36160	18 × 1786·66		
	8020 (1)	104984	$58\frac{3}{4}\times$ 1786·96 (25)	222·247 (15)	222 to 222·4
Li	0·338 (2)	11·58 (7)	$6\frac{1}{2}\times$ 1·782 (1)	7·017 (20)	7·03
Na	17·175 P	742·37	39 × 19·035	22·938	22·998 (2)
	17·260 S	746·03 (25)	39 × 19·134 (6)	22·999 (4)	
K	57·68 (1)	2928·7 (15)	53 × 55·259 (54)	39·082 (12)	39·097 (3)
Rb	237·60 (3)	12937·3 (50)	49 × 264·03 (9)	85·428 (15)	85·448 (5)
Cs	554·00 (2)	32565 (4·6)	51 × 638·53 (10)	132·852 (11)	132·823 (7)
Cu	248·444 (4)	7307·087 (150)	50 × 146·1419 (30)	63·5569 (60)	63·56 (1)
Ag	920·443 (5)	27789·10 (30)	66 × 421·0473 (45)	107·88	107·88
Au	3815·56 (2)	113934·9 (60)	81 × 1406·604 (70)	197·180 (19)	197·20 (7)
Mg'''	40·67 (7)	848·8 (14)	$39\frac{1}{2}\times$ 21·489		
	20·08 (1)	418·6 (2)	$19\frac{1}{2}\times$ 21·467		
	60·75 (7)	1267·4 (14)	59 × 21·481 (23)	24·367 (11)	24·362 (2)
Mg''	91·50 (3) S	1211·0 (5)	$56\frac{1}{4}\times$ 21·53	24·39 (4)	
	92·45 (3) D	1223·6 (5)	57 × 21·47	24·36 (4)	
Ca'''	105·883 (10)	2791·58 (75)	$48\frac{1}{4}\times$ 57·857		
	52·188 (10)	1371·14 (50)	$23\frac{1}{2}\times$ 58·346		
	158·071 (10)	4162·72 (100)	$71\frac{3}{4}\times$ 58·017 (14)	40·046 (4)	40·07
Ca''	222·88 (1)	3951·58 (80)	68 × 58·112 (15)	40·08 (1)	
r'''	394·22 (2)	11829·0	$42\frac{3}{4}\times$ 276·703 (40)		
	186·83 (3)	5528·7	$19\frac{3}{4}\times$ 279·933 (70)		
	581·03 (1)	17357·7 (16)	$62\frac{1}{2}\times$ 277·726 (33)	87·616 (51)	87·66 (3)
r''	801·88 (1)	16119·3 (7·4)	58 × 277·920	87·645 (190)	

TABLE XXIV.—*Continued.*

	ν.	$\Delta\nu$.	$m \times qw^2$.	Spectral atomic weight.	Chemical atomic weight.
Ba‴	878·14 (6)	29344·6 29518·7	43 × 682·432 43¼ × 682·506		
	370·56 (6)	11992·9 12062·37	17½ × 685·311 17½ × 689·298		
	1248·70 (6)	41337·5 (40) 41581·5	60½ × 683·265 (67) 60¾ × 684·468	137·427 (7) 137·548	137·43 (6)
Ba″	1690·93 (3)	38608·3 (180)	56½ × 683·332 (320)	137·433 (36)	
Ra″	4857·11	111056	60 × 1850·93	226·201	225·97 to 226·4
Zn‴	388·894	7204·19	46½ × 154·929		
	190·097	3486·29	22½ × 154·946		
	578·991 (10)	10690·48 (100)	69 × 154·934 (12)	65·4413 (20)	65·40 (3)
Zn″	872·8 (10)	9135 (13)	59 × 154·87 (23)	65·427 (45)	
Cd‴	1170·842 (8)	23105·83	50¾ × 455·278		
	542·00 (15)	10370·33	22¾ × 455·839		
	1712·84 (15)	33476·16 (300)	73½ × 455·458 (60)	112·2023 (80)	112·3 (1)
Cd″	2481·7 (6)	27348 (15)	60 × 455·48 (25)	112·200 (28)	
Eu‴	2630·30	51226	61½ × 832·92		
	2633·21	51281	61⅝ × 833·83		
	1003·87	18321	21½ × 852·14		
	1004·06	18323	21⅛ × 852·25		
	3634·17 (16)	69550	83 × 837·92	152·187 (70)	152·249
	3637·21 (16)	69604	83 × 838·60	152·249 (70)	
Eu″	5342·5 (10)	61207	73 × 838·45	152·24 (10)	
Hg‴	4630·467	87819·08	60¾ × 1445·581		
	1767·279	30008·03	20½ × 1463·806		
	6397·746 (10)	117827·11 (10)	81¼ × 1450·180 (100)	200·211 (8)	200·3 (3)
Al	112·038 (10)	1752·07 (30)	66 × 26·546 (2)	27·088 (2)	27·10 (5)
Ga	826·04 (5)	13540·7 (180)	77 × 175·857 (240)	69·720 (40)	69·9 (3)
In	2212·61 (30)	37687·5 (80)	79 × 477·056 (90)	114·831 (11)	114·8 (5)
Tl	7792·40 (30)	134153·46	89 × 1507·342 (150)	204·119 (10)	204·04 (5)
Sc	321 (?)	6407 (?)	91 × 70·41 (?)	44·114 (?)	44·1 (5)
O	3·65 (3)	171·0	18½ × 9·242		
	2·03 (2)	94·1	10¼ × 9·180		
	5·68 (3)	265·07	28¾ × 9·220 (40)	15·966 (40)	16
S	17·96 (15)	1044	28 × 37·28		
	11·21	651	17½ × 37·20		
	29·17 (20)	1695 (12)	45½ × 37·25 (20)	32·088 (100)	32·07 (?)
Se	103·680 (150)	6390	28¼ × 226·16		
	44·66 (250)	2736	12 × 227·98		
	148·34 (25)	9126	40¼ × 227·34	79·270 (280)	79·2 (?)
Mn	173·604 (50)	3420	31¼ × 109·44		
	129·263 (50)	2533	23¼ × 108·95		
	302·864 (50)	5953·32	54½ × 109·235	59·9512 (63)	59·93

There is no question but that the results now obtained by Hicks are extraordinarily accurate and that the hesitation in accepting this remarkable generalisation expressed previously must disappear, since it is obvious that the use of more accurate values for spectroscopic measures has materially improved the results.

It may be regarded as established that the oun enters definitely as a discrete quantity in the constitution of the spectra of an element, and in each case it is deducible from the data of the spectrum itself. The result is independent of the definite relation to the square of the atomic weight, although this relation was the means through which its existence was first discovered. The above table would seem to afford conclusive evidence in favour of this relation, nevertheless it involves the difficulty arising from the existence of isotopes. This difficulty arises in two ways; (1) if an "element" contains two or more isotopes always in the same proportion, the chemical atomic weight is the proportional mean of those of the isotopes, and an oun depending on that atomic weight would be meaningless; (2) if an element consisted of several isotopes we should expect its spectrum to be composed of lines belonging to each isotope. There is no doubt that the work of Hönigschmid, Soddy, and others has definitely established the existence of isotopes in the case of lead. Moreover, there is also found agreement between the spectra of ordinary lead and those of radioactive origin. Small differences in wave-lengths have, however, been found for five of the lines of lead by Merton,[1] who found for the wave-number differences of ordinary lead over radium lead the following values given in Table XXV. :—[2]

TABLE XXV.

λ.	Δn.
4058	0·065 ± 0·005
3740	0·053 ± 0·008
3684	0·035 ± 0·005
3640	0·052 ± 0·002
3573	0·037 ± 0·004

These are definite facts. How can they be squared with the other fact, namely, that the spectra so far analysed depend directly on the oun, itself depending on the atomic weight? Unfortunately the question cannot be dealt with directly, since no series have as yet been discovered for lead, nor has the oun been determined. In spite, however, of its incompleteness, the evidence points provisionally to practical equality in all the isotopes belonging to the same atomic number. If so, there must be some explanation for the two apparently irreconcilable facts. Hicks suggests the possibility that, of the different isotopes, one only is of normal type and that it alone is capable of emitting a spectrum, and that half helium atoms or hydrogen must be added or rejected in the others during the excitation before they can emit radiant energy.

[1] *Proc. Roy. Soc.*, A, **100**, 84 (1921).

[2] See also vol. ii., p. 230.

The evidence for the dependence of the oun on the square of the atomic weight would seem so remarkable as to exclude the supposition of any other relation. The difficulty would be avoided if it could be shown that the oun depended on the square of the atomic number. The weight relation is so closely followed and so many regularities are brought out where the quantity in question is 4 ouns that this is scarcely probable. Nevertheless the question is so important that it is desirable to test the data on this point. If it is found impossible, the impossibility of making the data fit will greatly add to the confidence felt in the positive result for the atomic weight. In making the calculations Hicks deals with the numbers $2z/100 = n$, where z is the atomic number. He points out that the results obtained show that the atomic number does not fit in with the conditions, that is to say, the evidence is definitely against the view that Δ is proportional to the square of the atomic number. Until further information is available the discussion of the difficulty raised by the existence of isotopes cannot be continued, and the matter for the present must remain *sub judice.*

The Relations Between the Spectra of the Elements of one Family.—Many attempts have been made from time to time to correlate the spectra of the elements which belong to one family of the periodic table, and it must be confessed that very small success has attended these efforts. Certain facts were pointed out by Kayser and Runge, and one of the most important is that in the case of the elements of the same family the constant wave-number differences of the pairs or the triplets are very nearly proportional to the squares of the atomic weights. In order to show this we may, with Rydberg,[1] compare the values of $\frac{1000\nu_1}{P^2}$, where P is the atomic weight; Table XXVI. contains the results.

TABLE XXVI.

	Na = 23·06	Mg = 24·38	Al = 27·08	O = 16
ν_1	17·19	40·91	112·02	3·70
$\frac{10^3\nu}{P^2}$	32·3	68·8	152·8	14·5
	K = 39·14	Ca = 40·00	Ga = 69·9	S = 32·06
ν_1	57·85	105·82	823·6	18·15
$\frac{10^3\nu_1}{P^2}$	37·8	66·1	168·6	17·7
	Rb = 85·44	Sr = 87·52	In = 113·4	Se = 79·07
ν_1	235·98	394·22	2212·54	103·7
$\frac{10^3\nu_1}{P^2}$	32·3	51·5	172·1	16·6
	Cs = 132·88	Ba = 137·04	Tl = 204·15	
ν_1	553·87	878·5	7792·63	
$\frac{10^3\nu_1}{P^2}$	31·6	46·8	187·0	

[1] *International Reports*, **2**, 217 (Paris, 1900).

Another interesting point Rydberg mentions in the same paper is, that if all the values of the expression $\frac{10^3\nu_1}{P^2}$ are plotted against the atomic weights P, a periodic curve is obtained and also an identically shaped periodic curve is obtained if the values of the common convergence limits of the first and second subordinate series are plotted instead of the expression $\frac{10^3\nu_1}{P^2}$.

Ritz [1] has shown that much closer values than the above are obtained if in place of $\frac{1000\nu_1}{P^2}$ we introduce $\frac{p_2 - p_1}{P^2}$; the discrepancies which still remain are probably due in part to the incompleteness of the series equations, but more especially to the fact that $(\pi_1 - \pi_2)^2$ is neglected, which is certainly not admissible in the case of aluminium, indium, and thallium. The values of $\frac{p_2 - p_1}{P^2}$ given by Ritz are set fourth in Table XXVII.

TABLE XXVII.

Sodium	14·2	Rubidium	18·0
Copper	18·6	Magnesium	14·6
Strontium	15·7	Cadmium	18·6
Aluminium	24·8	Thallium	32·7
Potassium	18·9	Cæsium	18·6
Silver	24·2	Calcium	17·7
Zinc	17·2	Mercury	22·3
Indium	29·2	Helium	20·4

Ramage [2] has published two papers on this subject, in the first of which he discusses the relations of the spectra, densities, and melting-points to atomic mass. Ramage carefully selects the lines which correspond in the spectra of analogous elements, that is to say, lines which have the same value of m in the equations to the series; the wave-numbers of these lines are then plotted against the squares of the atomic masses. When the corresponding points are joined together by lines, it will be found that these lines are mostly straight; there are, however, breaks in certain places, *e.g.* between sodium and potassium, and between magnesium and zinc. The diagram shows very clearly what was stated above, that ν varies with the square of the atomic weight; the lines connecting the corresponding members of homologous triplets and doublets intersect on the line of zero atomic mass.

Ramage gives an equation based on that deduced by Rydberg, by which can be calculated the wave-numbers of the principal series of potassium, rubidium, and cæsium; in Rydberg's equation he puts

$$n_0 + 35349 - 0{\cdot}2233W^2,$$

[1] *Phys. Zeitsch.*, **9**, 521 (1908).
[2] *Proc. Roy. Soc.*, **70**, 1, and 303 (1902).

where W is the atomic weight and

$$\mu = \{1{\cdot}19126 + 0{\cdot}00103W + (0{\cdot}04377 + 13W^2 \times 10^{-7})(1 - 3^{1-m})\}.$$

The last factor $(1 - 3^{1-m})$ is inserted to correct for a small variation in μ, which, he considers, occurs throughout the series. The wave-numbers obtained with this formula agree very closely with the observed values. In his second paper, Ramage gives similar equations for the subordinate series of these metals; the two convergence points of the first subordinate series are obtained from the equation

$$n_0 = 22830 - 21{\cdot}633W \pm \frac{A}{2},$$

where W is the atomic weight and A is the average distance between the doublets. This distance he takes to be 57·8, 236·4, and 547·6 for potassium, rubidium, and cæsium respectively. The wave-numbers of the lines of the series can be obtained from the equation of Rydberg by putting $\mu = 0{\cdot}7869 - (1466W^2 \times 10^{-8})$; the results calculated in this way are very near the observed values. For the second subordinate series Ramage finds

$$n_0 = 22850 - 21{\cdot}812W \pm \frac{B}{2}$$

and

$$\mu = 0{\cdot}7990 + 7784W^2 \times 10^{-9},$$

where B = 57·8, 238·0, and 553·6 for potassium, rubidium, and cæsium, respectively. The values of the convergence limits of the two series as obtained by Ramage with the various methods are compared in Table XXVIII.

TABLE XXVIII.

Element.	From above formulæ.			By calculation from observed lines.	From formula for principal series.	Rydberg's[1] values.
	First series	Second series.	Mean of two series.	mean.		
Potassium (1)	21953·9	21968·0	21960·95	21960	21969·4	21955·46
,, (2)	22011·7	22025·8	22018·75	22018	22024·3	22013·31
Rubidium (1)	20861·8	20868·3	20865·65	20865	20868·6	20869·15
,, (2)	21098·2	21106·3	21102·25	22101	21112·3	21098·83
Cæsium (1)	19677·2	19674·2	19675·7	19672	19686·7	—
,, (2)	20224·8	20228·0	20226·4	20226	20234·2	—

The numbers in the sixth column were obtained by the Rydberg-Schuster law, which connects the principal and subordinate series.

Marshall Watts[2] has drawn attention to interesting relationships between the spectra of analogous metals and the squares of their atomic weights. He finds that there are two distinct kinds of

[1] *Paris Reports*, **2**, 212 (1900).

[2] *Phil. Mag.*, **5**, 203 (1903).

connection between the spectra of allied elements. In one class, to which zinc, cadmium, and mercury, and gallium and indium belong, the differences between the wave-numbers of certain lines of the one element are to the differences between the wave-numbers of the corresponding lines of the other element as the squares of their atomic weights. It is thus possible to calculate the atomic weight of one element from the atomic weight of another of the same family by means of their spectra. In the other class of cases to which the alkali metals and those of the alkaline earths belong, the element of greater atomic weight has the smaller wave-number; three elements are so related that the wave-number differences between the elements, in comparing corresponding lines in their spectra, are proportional to the differences between the squares of the atomic weights. It is thus possible in this case to calculate the atomic weight of one element from the atomic weights of two other elements in the same series.

An example may be given from the two classes in order to show the accuracy.

Example 1.—Determination of the atomic weight of zinc (64·9) from that of cadmium (111·83).

The following are the wave-numbers of the lines assumed to correspond :—

	Cadmium.		Zinc.	
(*a*)	30654·4	10*r*	32500·0	8*r*
(*b*)	30734·9	8*b*	32540·1	10*r*
(*c*)	31905·5	8*b*	32928·7	10*b*
(*d*)	32446·8	6*b*	33118·6	8*b*
(*e*)	36023·7	6*b*	34310·8	4
(*f*)	37334·5	8	34791·3	6
(*g*)	38851·1	4	35285·7	8*r*
(*h*)	39280·5	2*n*	35408·9	6
(*i*)	43690·5	10*r*	36934·7	6
(*j*)	44086·7	4*r*	37059·2	2*b*
(*k*)	44630·0	6*r*	37242·2	8*b*
(*l*)	45550·6	1	37548·1	8

From these numbers we get for the atomic weight of zinc by combining

(*a*)	and	(*c*)	65·44
(*a*)	,,	(*d*)	65·69
(*a*)	,,	(*f*)	65·48
(*a*)	,,	(*g*)	65·17
(*a*)	,,	(*h*)	64·93
(*a*)	,,	(*i*)	65·28
(*a*)	,,	(*j*)	65·15
(*a*)	,,	(*k*)	65·12
(*a*)	,,	(*l*)	65·16
(*b*)	,,	(*e*)	64·69
(*c*)	,,	(*e*)	64·77, and so on.

	Cadmium.		Zinc.	
(*m*)	19655·8	10*r*	21170·0	10*r*
(*n*)	20826·7	10*r*	21591·6	8*b*
(*o*)	28840·2	10*r*	24371·4	2
(*p*)	30301·9	4	24869·7	4

(*m*) and (*n*) 67·08
(*n*) ,, (*o*) 65·38
(*n*) ,, (*p*) 65·76
(*m*) ,, (*p*) 65·98

	Cadmium.		Zinc.	
(*q*)	27669·1	8*r*	29885·1	10*r*
(*r*)	29370·4	10*r*	30456·0	8*r*

(*q*) and (*r*) give 64·78 for the atomic weight of zinc.

Example 2.—From the atomic weight of cæsium, 132·7, and that of potassium to calculate the atomic weight of rubidium (85·2).

The following lines are assumed to correspond :—

	Cæsium.		Rubidium.		Potassium.	
(*a*)	12469	6	13742	4	14465	7
(*b*)	21764	6*r*	23714	6*r*	24700	6*r*
(*c*)	21945	8*r*	23791	8*r*	24719	8*r*
(*d*)	25707	4*r*	27833	4*r*	28998	6*r*
(*e*)	25787	6*r*	27868	6*r*	29006	8*r*
(*f*)	27638	2*r*	29832	2*r*	31068	4*r*
(*g*)	27678	4*r*	29852	4*r*	31073	6*r*

(*a*) gives 86·87
(*b*) ,, 83·24
(*c*) ,, 83·11
(*d*) ,, 84·51
(*e*) ,, 84·93
(*f*) ,, 85·52
(*g*) ,, 85·51

Runge and Precht [1] determined the atomic weight of radium by comparing the constant wave-number difference of the pairs in the first and second subordinate series with those in the cases of magnesium, calcium, strontium, and barium. It has been stated before that this constant wave-number difference, which is the same as in the first pair of the principal series, is proportional to the squares of the atomic weights of the elements in one family. This, however, according to Runge and Precht, is not strictly true, but the atomic weight is proportional to a power of the wave-number difference, or the logarithms of the atomic weights are a linear function of the logarithms of the wave-number differences. Now, radium belongs to the same family as magnesium, calcium, strontium, and barium, whose constant

[1] *Phys. Zeitsch.*, **4**, 285 (1903).

wave-number differences are 9·17, 223, 801, and 1691 respectively. On plotting the logarithms of these numbers against the logarithms of the atomic weights, a straight line was drawn through the points and extrapolated to find the atomic weight of radium, taking its wave-number difference as 4858·6. The atomic weight in this way was found to be 257·8. Against this, however, is the experimentally determined number 226, which is known to be very close to the truth.

On the other hand, Marshall Watts [1] has drawn the curves for four different families, and finds that the lines are not straight but are slightly curved; the effect of this curvature being especially noticeable in the case of the elements of the highest atomic weight. From the curve of the alkaline earths he has calculated an interpolation formula which gives the atomic weights as follows: Magnesium, 24·52; calcium, 40·08; strontium, 87·62; barium, 137·41; and radium, 226·56, from which latter number it may be concluded that the spectrum data are quite consistent with the atomic weight found for radium by chemical methods.

Since from the point of view of series spectra the atomic numbers have a greater importance than the atomic weights, various attempts have been made to prove a connection between these and doublet or triplet separations. For example, Ives and Stuhlmann [2] found that slightly better results were obtained if atomic numbers were used in place of atomic weights in Runge and Precht's method of correlation. Once again, however, was an incorrect value obtained for radium, since the atomic number was calculated to be 96, the true value being 88. Anslow and Howell [3] plotted the logarithms of the wave-number differences between the extreme members of the triplets of the same group against the logarithms of the atomic numbers and obtained a straight line. In the case of the calcium group this indicated 87 as the atomic number of radium.

It may be concluded that there is no satisfactory correlation between spectra and atomic weights or atomic numbers for members of the same family. Indeed, the only relation of any value which has been established is that of Hicks, but the physical significance of this is very obscure. As will be shown later there is a much closer connection between the enhanced spectra of an element and the arc spectra of those elements which precede it in descending order of atomic numbers, a connection predicted by Kossel and Sommerfeld in their law of spectroscopic displacement.

Nicholson's Development of the Rydberg Formula. An interesting paper has been published by Nicholson,[4] in which he discusses the relative merits of the formulæ of Rydberg, Ritz, and Hicks. He points out that the various formulæ, in particular those of Ritz and Hicks, fit the wave-lengths almost equally well, and all demonstrate at least the approximate truth of two fundamental

[1] *Phil. Mag.*, **18**, 411 (1909). [2] *Phys. Rev.*, **5**, 368 (1915).
[3] *Proc. Nat. Acad. Sci.*, Washington, **3**, 409 (1917).
[4] *Proc. Roy. Soc.*, A, **91**, 255 (1915).

results, namely, (1) that the diffuse and sharp series have the same limits, and (2) the Rydberg-Schuster law. Then there is further the question as to the fixed value of Rydberg's constant. Hicks, basing his evidence on the earlier measurements of helium, concluded that the last is not the same for helium and hydrogen.

The general formula for any series is

$$n = \mathrm{A} - \mathrm{N}/(\mathrm{D}_m)^2$$

where
$$\mathrm{D} = m + \mu + \alpha/m \quad . \quad . \quad . \quad \text{Hicks (1)}$$
$$\mathrm{D} = m + \mu + \beta/m^2 \quad . \quad . \quad \text{Ritz (2)}$$

In general the results given by (1) are superior to those given by (2), but as shown on p. 26 the formula on which Ritz relied is of the form

$$n = \mathrm{A} - \mathrm{N}/[m + \mu + \alpha(\mathrm{A} - n)]^2 \quad . \quad . \quad . \quad (3)$$

so that the superiority of (1) over (2) is not a conclusive test of the Ritz formula.

In the first place, Nicholson devises a method for the accurate determination of the limits of series and for this purpose he uses the formulæ for helium given by Hicks.[1] In the case of the diffuse series (more refrangible component) the formula is

$$n = 29222{\cdot}595 - 109689{\cdot}2/(m + 0{\cdot}996347 + 0{\cdot}002200/m)^2$$

and hence these lines can be represented by

$$n = \mathrm{A} - \mathrm{N}/(m + 1 + \delta)^2,$$

where δ never exceeds 0·004. If this be expanded we have

$$n = \mathrm{A} - \frac{\mathrm{N}}{(m+1)^2}\left[1 - \frac{2\delta}{m+1} + \frac{3\delta^2}{(m+1)^2} \cdots\right]$$

The fourth term of this very convergent series is $3\mathrm{N}\delta^2/(m+1)^4$, and since N is about 10^5, it cannot exceed $3 \times 10^5 \times 16 \times 10^{-6} \times 3^{-4} = 0{\cdot}06$, when $m = 2$. For all lines beyond $m = 3$ it cannot exceed 0·007, so that for all these lines we may put

$$n = \mathrm{A} - \mathrm{N}/(m+1)^2 + 2\mathrm{N}\delta/(m+1)^3,$$

or
$$(m+1)^3 n = \mathrm{A}(m+1)^3 - \mathrm{N}(m+1) + 2\mathrm{N}\delta$$
$$(m+2)^3 n = \mathrm{A}(m+2)^3 - \mathrm{N}(m+2) + 2\mathrm{N}\delta$$
$$(m+3)^3 n = \mathrm{A}(m+3)^3 - \mathrm{N}(m+3) + 2\mathrm{N}\delta$$

and
$$\mathrm{A} = \frac{(m+2)^3 n_{m+1} - (m+1)^3 n_m + \mathrm{N}}{(m+2)^3 - (m+1)^3}.$$

If N were known, this formula would permit a determination of the limit of the series from any pair of consecutive lines. Although the exact value of N is one of the objects of the investigation, yet we know both on the definite theory of Bohr and on Hicks's calculations that

[1] *Phil. Trans.*, A, **210**, 102 (1911).

it cannot differ from Curtis' value for hydrogen. We may therefore put

$$N = 109679{\cdot}22 + dN,$$

where dN has a small unknown magnitude.[1]

From the Hicks formula for the sharp series of helium,

$$n = 29222{\cdot}696 - 109719{\cdot}6/(m + 0{\cdot}705092 - 0{\cdot}013408/m)^2,$$

using the same methods as above, Nicholson finds for all lines above $m = 3$

$$A = \frac{(m + 1{\cdot}7)^3 n_{m+1} - (m + 0{\cdot}7)^3 n_m + N}{(m + 1{\cdot}7)^3 - (m + 0{\cdot}7)^3}.$$

Similarly from Hicks's formula for the principal series he finds for all lines above $m = 2$

$$A = \frac{(m + 2{\cdot}93)^3 n_{m+2} - (m + 1{\cdot}93) n^3{}_{m+1} + N}{(m + 2{\cdot}93)^3 - (m + 1{\cdot}93)^3}.$$

From these three equations Nicholson calculates the three limits and obtains the following mean values:—

$$\begin{aligned} A &= 29223{\cdot}776 + 0{\cdot}004416\,dN \quad \text{(diffuse)},\\ A' &= 29223{\cdot}780 + 0{\cdot}00468\,dN' \quad \text{(sharp)},\\ A'' &= 38454{\cdot}943 + 0{\cdot}00622\,dN'' \quad \text{(principal)}. \end{aligned}$$

If Curtis' value for N be used, or if N is an absolute constant for arc spectra, $dN = dN' + dN''$ and $A = A'$ with extraordinary accuracy, so that the sharp and diffuse limits are identical. By the Rydberg-Schuster law

$$P(1) = 38454{\cdot}943 - 29223{\cdot}780 = 9231{\cdot}163,$$

the measured value being 9231·198. The agreement is almost exact, and the fact that both laws are fulfilled so exactly is a convincing argument for a belief in both and in Curtis' value of N being true for helium. It may be pointed out that Hicks's formulæ for the sharp and diffuse series gave a difference of 0·1 between the limits for the two series.

Nicholson next investigates the best form of the function $D_m{}^2$ in the general equation

$$n = A - N/D_m{}^2.$$

Taking first the sharp series he calculates the value of dN and using the Hicks formula (1), in which

$$D = m + \mu + \alpha/m,$$

he finds that $dN = 194{\cdot}3$, which is too large. With the Ritz approximate formula $dN = -255{\cdot}2$, which confirms previous experience as

[1] This is the value given by Curtis in his first paper. His later value, given on p. 39, is 109678·3.

regards the superiority of the Hicks formula. On the other hand, the proper Ritz formula gives $dN = 86{\cdot}7$, which is nearer the accepted limits of variation in N. This formula, therefore, is superior to the previous two, which must modify the statement made by Hicks that his formula is superior to that of Ritz, in view of the fact that he did not test the proper Ritz formula.

Nicholson then tries formulæ with three constants, and he first takes the Hicks formula with another term,

$$D = m + \mu + \alpha/m + \beta/m^2,$$

and finds that dN is then 165·8 and that, with the addition of yet another term, γ/m^3, $dN = 20{\cdot}4$. Clearly, therefore, with the Hicks formula and more constants dN is converging to a small value, but the convergence is slow and the number of constants already contained indicates that the formula is not of the best type.

On the other hand, Rydberg suggested that $D_m{}^2$ is a function of $m + \mu$ and the more probable type is, therefore,

$$D_m = m + \mu + \alpha/(m + \mu) + \beta/(m + \mu)^2,$$

and using this formula Nicholson finds that $dN = -2{\cdot}38$. The value of μ is 0·700056 and consequently it seems clear that μ is converging to 0·7 while dN is converging to zero.

Since he obtains the same result, namely, that $dN = 0$, by applying the Rydberg formula to the diffuse and principal series of helium, Nicholson finally concludes that

1. N is an absolute constant for hydrogen, helium, and all arc spectra and has the Curtis value 109678·3.
2. The helium series can best be expressed by an extension of the Rydberg formula—

$$n = A - N/[m + \mu + \alpha/(m + \mu) + \beta/(m + \mu)^2 + \ldots]^2.$$

3. The Rydberg-Schuster law is exact for helium.

This conclusion would seem to be of considerable importance and the accurate representation of the helium lines by the extension of Rydberg's formula is of great interest, since it undoubtedly suggests that this formula is of the right type. Again, his method of calculating the convergence limit gives a more definite proof of the validity of the Rydberg-Schuster law than had previously been obtained. With regard to the conclusion that N is an absolute constant for the arc spectra of hydrogen and helium, this does not agree with Bohr's theory, since this leads to a small change in N with increase in the atomic weight, a change which has been experimentally found by Fowler in his work on the enhanced line series of helium, and later confirmed in the case of other elements.

After the foregoing account of work on spectral series, which may be looked upon as preliminary, we may next turn to the Bohr theory and its consequences. All that we have done at present is to review the general principles of series architecture in its simplest form, and

at the same time to discuss the three series formulæ put forward by Rydberg, Ritz, and Hicks. The discussion of these formulæ was a necessity, for the Bohr theory has not as yet given a true physical formula except in the case of the hydrogen spectrum and the enhanced spectrum of helium. Consequently, in any work on the apportionment of lines to their series one of these three formulæ must still be used.

The Bohr Theory.—In seeking for an explanation of the fact that the emission spectra of atoms consist of discrete radiations and that the wave-numbers of these can, at any rate in the case of the elements of low atomic weight, be expressed by simple formulæ such as those of Rydberg and Ritz, Bohr took as the basis of his calculations the structure of the atom proposed by Rutherford. According to this conception an elementary atom consists of a positively charged nucleus with a number of electrons revolving in closed orbits round it, the number of the electrons being sufficient to neutralise the positive charge on the nucleus. Rutherford calculated that the positive charge on the nucleus corresponded to a number of electrons which is equal to about half the atomic weight, and so it is assumed that the number of electrons is equal to the atomic number.

The hydrogen atom may be assumed to consist of one electron revolving round a nucleus of equal and opposite charge, the mass of the nucleus being very large compared with that of the electron. Bohr points out that, if at the outset the mass of the nucleus be assumed to be infinitely large compared with that of the electron, and if for the moment the energy radiation be disregarded which will, according to the ordinary laws of electrodynamics, accompany the accelerated motion of the electron, the orbit of the electron in accordance with Kepler's first law will be an ellipse with the nucleus in one of the foci. If ω be the frequency of revolution, $2a$ be the major axis of the ellipse, e the charge on the electron, m its mass, and W the work which must be added in order to remove the electron to an infinite distance from the nucleus, then

$$\omega^2 = \frac{2W^3}{\pi^2 e^4 m} \quad \text{and} \quad 2a = \frac{e^2}{W}. \qquad . \qquad . \qquad . \qquad (1)$$

The frequency of revolution and the length of the major axis, therefore, only depend on W and are independent of the eccentricity, and hence by changing W all possible values for ω and $2a$ may be obtained. It is obvious, however, from the fact that the system is characterised by a spectrum of lines that the orbit of the electron cannot possibly take on all values. Again, any attempt to explain the radiation of energy by the system according to the ordinary laws of electrodynamics will only make matters worse, since any loss of energy will increase W and by the above equations ω will increase and $2a$ decrease. There is no reason why this process should stop until the nucleus and electron approach one another so closely that they no longer attract one another.

It is, therefore, impossible to make any headway with the Rutherford atomic model as long as the classical laws of electrodynamics only are applied. As is well known a similar conclusion was arrived at from the study of temperature radiation, and the difficulties were surmounted by Planck who made the new assumption that a system of oscillating electrically charged particles do not radiate nor absorb energy continuously, but discontinuously. Briefly, the new assumption means that at any moment the system contains an amount of energy which is always equal to an integral multiple of a definite quantum of energy, $h\nu$, where h is a constant (known as Planck's constant) and ν is the oscillation frequency of the system. Any gain or loss of energy by the system will therefore be equal to one or more quanta characteristic of that system. The question arises as to whether the difficulties found with the Rutherford atomic model can be surmounted by the application of the Planck concept of energy quanta.

It is evident that the Planck theory cannot be applied directly, since it deals with the absorption and radiation of energy by a system of electrical particles having a definite oscillation frequency, which depends only on the nature of the system and is independent of the energy content. In the case of the Rutherford model, on the other hand, equations (1) show that the frequency of revolution ω depends on the energy of the system. We can, however, make use of the Planck concept of the energy quantum and assume that when an element exhibits a spectral line of frequency ν one of the atoms can radiate a single energy quantum $h\nu$. Further, the energy content of the atom is decreased, and, if E_1 and E_2 are the energy contents before and after the energy radiation, we have

$$h\nu = E_1 - E_2$$

and

$$\nu = E_1/h - E_2/h \quad . \quad . \quad . \quad . \quad (2)$$

Bohr calls the energy conditions represented by E_1 and E_2 stationary states, indicating thereby that they form waiting places between which occurs the emission of the energy corresponding to the spectral lines. The Ritz combination principle (see p. 27) can be written in the form

$$1/\lambda = F_n(n) - F_n(n') \quad . \quad . \quad . \quad . \quad (3)$$

where n and n' are whole numbers and $F_n(n)$ and $F_n(n')$ are series of functions of n which may be written approximately

$$F_n(n) = N/(n + \alpha)^2,$$

where N is Rydberg's constant and α is a constant which differs for the different functions. Since $\nu = v/\lambda$, where v is the velocity of light, we have

$$\nu = vF_n(n) - vF_n(n') \quad . \quad . \quad . \quad . \quad (3')$$

Comparing (2) and (3') a spectral line may be regarded as being emitted by the transition of an atom between two stationary states

in which the energy, apart from an additive arbitrary constant, is given by $-vn\mathrm{F}_n(n)$ and $-vh\mathrm{F}_n(n')$, respectively. The negative sign is used because the energy of the atom is most simply characterised by the work required to remove the electron completely from the atom. On this interpretation the combination principle states that a series of stationary states exists for a given system, and that in passing from one to any other of these states the system radiates a monochromatic radiation.

Bohr next applies the above conception to the case of the hydrogen atom. The spectral lines are given (see p. 20) by the general formula

$$1/\lambda = \mathrm{N}\left(\frac{1}{n^2} - \frac{1}{n'^2}\right)$$

or

$$\nu = v\mathrm{N}\left(\frac{1}{n^2} - \frac{1}{n'^2}\right) \quad . \quad . \quad . \quad . \quad (4)$$

The spectral lines have been assumed to be given by the transitions between a series of stationary states, and the energy of the system in the nth state, apart from an additive constant, is given by $-\mathrm{N}h\nu/n^2$. It may be assumed that in calculating the frequency of revolution of the electron the formula (1) may be used and if for the nth stationary state we put $\mathrm{W} = \mathrm{N}h\nu/n^2$ we have

$$\omega_n{}^2 = \frac{2}{\pi^2} \cdot \frac{\mathrm{N}^3 h^3 v^3}{e^4 m n^6} \quad \text{and} \quad 2a_n = \frac{n^2 e^2}{h\mathrm{N}} \quad . \quad . \quad (5)$$

From the general equation (4) the frequency of the radiation when the system passes from the $(n+1)$th state to the nth stationary state is

$$\nu = v\mathrm{N}\left(\frac{1}{n^2} - \frac{1}{(n+1)^2}\right),$$

and if n is very large $\nu = 2v\mathrm{N}/n^3$ approximately. This frequency may be put equal to the frequency of revolution and so we have

$$\omega_n = 2v\mathrm{N}/n^3 \quad . \quad . \quad . \quad . \quad (6)$$

Introducing this value of ω_n into equation (5) it will be seen that n disappears and the equation is only satisfied when

$$\mathrm{N} = \frac{2\pi^2 e^4 m}{vh^3} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Now the value of N is accurately known for hydrogen and has the value 109678·3 when wave-numbers are used, and if we take Millikan's values,

$$e = 4{\cdot}774 \times 10^{-10},$$
$$h = 6{\cdot}545 \times 10^{-27},$$
$$e/m = 1{\cdot}767 \times 10^{7}.$$

The value of N is found from (7) to be $3{\cdot}292 \times 10^{15}$ for oscillation frequencies, or $1{\cdot}0978 \times 10^{5}$ for wave-numbers, which is remarkably close to the known value.

This agreement clearly gives a close connection between the spectrum and the Rutherford atomic model of hydrogen. Moreover, the line spectrum of hydrogen should contain no other lines than those given by the formula

$$1/\lambda = \frac{N}{n^2} - \frac{N}{n'^2},$$

and consequently considerable doubt was thrown on the authenticity of the lines discovered by Pickering and calculated by Rydberg as hydrogen lines. Bohr pointed out that these lines can be explained in another way, on the supposition that they are due not to hydrogen, but to some other simple system consisting of a single electron revolving round a nucleus having a charge xe. The expression for ω in (1) becomes

$$\omega^2 = \frac{2W^3}{\pi^2 x^2 e^4 m}$$

and the system will emit a spectrum, the wave-numbers of the lines being given by

$$1/\lambda = \frac{2\pi^2 x^2 e^4 m}{vh^3}\left(\frac{1}{n^2} - \frac{1}{n'^2}\right) = N\left(\frac{1}{\left(\frac{n}{x}\right)^2} - \frac{1}{\left(\frac{n'}{x}\right)^2}\right) \quad . \quad (8)$$

A comparison of this formula with those for the Pickering and Rydberg series shows that the lines can be explained, if it be assumed that they are due to an electron revolving round a nucleus having a charge $2e$, or according to Rutherford's theory round a nucleus of a helium atom. It follows therefore that these series can be combined in a general formula—

$$1/\lambda = 4N(1/n^2 - 1/n'^2).$$

It must be remembered that in the hydrogen spectrum the emission of spectral radiations is due to the changes in the orbit of the single electron in revolution round the nucleus with charge e. In the case of the helium atom the nuclear charge of $2e$ means that both electrons have been displaced and only one of these moves to different orbits on its return. We have, therefore, two types of spectral series for helium, one of which is expressed by a formula involving N and the other by a formula involving 4N. The second type is usually denoted as the spectrum of ionised helium or He^+.

From his measurements Fowler found the ratio of N for ionised helium and hydrogen to be 4·001638, which differs from 4 by an amount too large to be accounted for by experimental error. In all the preceding it has been assumed that the mass of the nucleus is infinitely large compared with that of the electron, but this is of course not true. For a hydrogen atom the ratio M/m is 1845 and for helium it is about 7261·5. Bohr shows that if the ratio of the masses of nucleus and electron is M/m the value of N will be $N\left(\frac{M + m}{Mm}\right)$.

From this it follows that the ratio of N for ionised helium to N for hydrogen is

$$\frac{4M_{He}(M_H + m)}{M_H(M_{He} + m)} = 4{\cdot}001626$$

which is exceedingly close to Fowler's observed value.

The applicability of the general formula (8) to ionised elements has more recently been established by Fowler, and this will be discussed below when the series of enhanced lines are dealt with.

According to Bohr's theory the value of N will be different for different elements and if N_∞ be the value of N when $M/m = \infty$, then in the case of an element having an atomic weight of A we will have

$$N_A = N_\infty\left(\frac{Mm}{M + m}\right).$$

The value of N for hydrogen has been found by Curtis [1] to be 109768·3 and consequently for neutral helium N = 1097229, for lithium N = 109729·25, whilst N_∞ = 109737·7. Birge,[2] basing his calculations on the fine line structure has found the value of N for hydrogen to be 109677·7 ± 0·2 and N_∞ to be 109736·9 ± 0·2. For the spectra of elements of greater atomic weight than helium the exact value of N is of less importance, since the series formulæ used in expressing the series are only approximate.

There is no doubt that the Bohr theory offers a physical explanation of the existence of spectral series and that in the two simplest cases, namely, those of hydrogen and ionised helium, the wave-numbers of the various series are given by the general formula

$$1/\lambda = \frac{2\pi^2x^2e^4m}{vh^3}\left(\frac{1}{n^2} - \frac{1}{n'^2}\right) = x^2N\left(\frac{1}{n^2} - \frac{1}{n'^2}\right)$$

where xe is the charge on the nucleus, n is an integer, and $n' = n + 1$, $n + 2$, $n + 3$, etc. The limits of the series are given by $n' = \infty$. For the more complex spectra n and n' are no longer integers and we have the general formula of the type

$$1/\lambda = \frac{2\pi^2x^2e^4m}{vh^3}\left[\frac{1}{(n+\mu_1)^2} - \frac{1}{(n'+\mu_2)^2}\right] = x^2N\left[\frac{1}{(n+\mu_1)^2} - \frac{1}{(n'+\mu_2)^2}\right] \quad (9)$$

using Rydberg's formula as the simplest.

Attention may be drawn to the confirmation which this theory gives of the main contentions upheld by Rydberg in putting forward his theory. In the first place, we find complete justification for his conviction that N is a universal constant for all elements, the minor variations calculated by Bohr being of relatively small importance. In the second place, the essential basis of his theory was that the wave-numbers of the lines in a given series are given by the

[1] *Proc. Roy. Soc.*, A, **90**, 605 (1914); **96**, 147 (1919). See also p. 39.
[2] *Phys. Rev.*, **17**, 589 (1921).

differences between a constant term (the limit of the series) and a term which varies by adding consecutive integers to n in the expression $N/(n+\mu)^2$. In the third place, we have the Rydberg-Schuster law. Although we now know that in actual fact a series is expressed more closely by the Ritz and Hicks formulæ than by the Rydberg formula, this in no way detracts from the brilliance of Rydberg's pioneer work.

The Bohr theory suggests a very instructive method of plotting spectral series which gives a diagrammatic scheme of the various electron orbits and was employed by Fowler.[1] The method may be illustrated by hydrogen for which the general equation for wave-numbers is

$$1/\lambda = N\left(\frac{1}{n^2} - \frac{1}{n'^2}\right)$$

where n and n' are integers. The values of $N/1^2$, $N/2^2$, $N/3^2$, etc., are calculated and their logarithms are plotted on a linear scale, the logarithms being used in place of the numbers in order to obtain

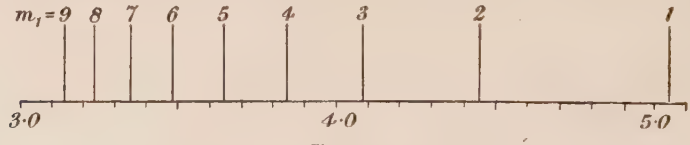

FIG. 2.

(*From Fowler's "Report on Series in Line Spectra." Fleetway Press.*)

a better spacing. The values with N = 109768·3 are given in Table XXIX.

TABLE XXIX.

m.	$\frac{N}{n^2}$.	$\log \frac{N}{n^2}$.
1	109678·3	5·0401207
2	27419·6	4·4380607
3	12185·9	4·0858581
4	6854·9	3·8360007
5	4387·2	3·6421807
6	3046·6	3·4838181
7	2238·3	3·3499247
8	1713·7	3·2339407
9	1354·1	3·1316357
10	1097·7	3·0401207

The numbers in the third column are plotted on a linear scale as shown in Fig. 2. The lines may be taken as representing the non-radiating orbits, the line 1 being the innermost orbit and the nucleus being situated somewhere on the right-hand side of the diagram. A spectrum line is radiated when an electron in one of the orbits on the

[1] *Report on Series in Line Spectra*, p. 66.

left falls on one of the orbits on the right, and the wave-number of the line is given by the difference between the values of N/n^2 for the two orbits. Thus, the Balmer series is given by the return of the electron, which has been displaced by the action of the discharge, to orbit 2. The first line of the series ($\lambda = 6562{\cdot}79$) is produced when the electron, having been displaced to orbit 3, returns to orbit 2, the wave-number being $27419{\cdot}6 - 12185{\cdot}9 = 17233{\cdot}7$. The second line is given by the return of the electron from orbit 4 to orbit 2, and so on, the limit of the series being given by the return of the electron from infinite distance to orbit 2. Other possibilities are given by the return of the electron from orbits 2, 3, 4, etc., to orbit 1, which gives the Lyman series in the very short wave ultra-violet, and by the return of the electron from orbits 4, 5, etc., to orbit 3, two lines of which have been observed in the infra-red. The limits of these two series, given by the return of the electron from infinity, are $n = 109768{\cdot}3$ and $12185{\cdot}9$ or $\lambda = 911{\cdot}76$ and $8206{\cdot}2$ respectively.

The value of this method of plotting is well shown by the case of sodium where there are four series, namely, the principal, sharp, diffuse, and fundamental. The series formula used in expressing the

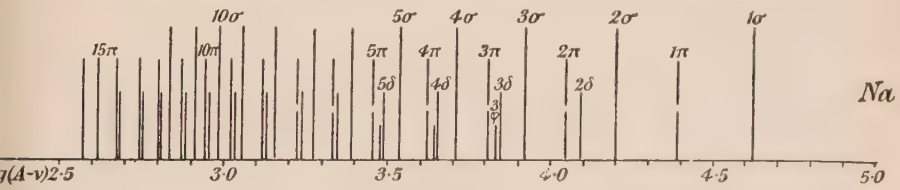

FIG. 3.

(From Fowler's "Report on Series in Line Spectra." Fleetway Press.)

wave-numbers is that of Hicks (see p. 40), $1/\lambda = A - N/(m+\mu+\alpha/m)^2$, and the values of the variable terms of the four series are given in Table XXX., it being remembered that the principal series consists of doublets with decreasing differences in wave-numbers, whilst the sharp and diffuse series consist of doublets with constant wave-number difference.

The logarithms of these values plotted on a linear scale are shown in Fig. 3, the different series being indicated by lines of different lengths and the double values of the principal series being indicated by a break in the lines. The innermost orbit is the 1σ orbit and the falls of the electron from the closely adjacent π_1 and π_2 orbits give the principal series of doublets with diminishing separation, the general formulæ being $1\sigma_1 - m\pi_1$ and $1\sigma_1 - m\pi_2$. The falls from the σ and δ orbits to the adjacent $1\pi_1$ and $1\pi_2$ orbits give the sharp and diffuse series of doublets with constant separation, the general formulæ being

$$\left.\begin{aligned} 1/\lambda &= 1\pi_1 - m\sigma \\ 1/\lambda &= 1\pi_2 - m\sigma \end{aligned}\right\} \text{sharp series,}$$

$$\left.\begin{aligned} 1/\lambda &= 1\pi_1 - m\delta \\ 1/\lambda &= 1\pi_2 - m\delta \end{aligned}\right\} \text{diffuse series.}$$

TABLE XXX.

m.	Principal.	Sharp.	Diffuse.	Fundamental.
1	24475·85 24492·83	41449·00 —	— —	— —
2	11176·14 11181·63	15709·50 —	12276·16 —	— —
3	6406·34 6408·33	8248·28 —	6900·35 —	6860·37 —
4	4151·30 4152·80	5077·31 —	4412·47 —	4390·37 —
5	2907·46 2908·93	3437·28 —	3061·92 —	3041·5 —
6	2149·80 2150·69	2480·65 —	2248·56 —	— —
7	1654·08 1655·31	1874·49 —	1720·88 —	— —
8	1312·28	1466·0	1357·2	—
9	1065·86	1175·5	1098·7	—
10	883·40	966·1	907·1	—
11	743·31	804·4	761·7	—
12	634·92	679·5	647·7	—
13	548·13	—	559·0	—
14	478·59	—	491·0	—
15	421·10	—	—	—

The fundamental series, $1/\lambda = 2\delta - m\phi$, is given by the fall of the electron from the ϕ orbits to the 2δ orbit. In addition to these there are a great number of electron falls which are possible, many of which take place since lines corresponding to them have been observed. Thus there are falls from the outer π and the ϕ orbits to $1\pi_1$ and $1\pi_2$, falls from orbits 2π to orbits 2σ and 2δ, etc. In this way with 51 orbits 100 lines have been accounted for in the sodium spectrum.[1]

Ionisation and Resonance Potentials.—There is an obvious deduction to be made from Bohr's theory, since we may consider the

[1] More recent developments have indicated that certain definite restrictions normally exist which govern the possible electron jumps. These are dealt with below.

amount of energy which is required to shift the electron from its normal orbit to the outer orbit, during the return from which the spectral line is radiated. It is well known that atoms can be ionised by the impact of electrons from other atoms, and since the kinetic energy of these can be measured at once we have a method of applying an independent test to the Bohr theory. It has already been shown that the energy characteristic of the stationary orbits of hydrogen is given by

$$W_n = 2\pi^2 me^4/n^2h^2,$$

where n is the integer defining the orbit, and this is the energy required to remove the electron to an infinite distance from the nucleus, that is to ionise the atom.

Since

$$N = 2\pi^2 e^4 m/vh^3$$
$$W_n = vhN/n^2.$$

When the electron falls from one orbit to another we have

$$h\nu = W_n - W_{n'} = vhN(1/n^2 - 1/n'^2)$$

or for series spectra in general, using Rydberg's formula,

$$h\nu = W_n - W_{n'} = vhN[1/(n + \mu_1)^2 - 1/(n' + \mu_2)^2].$$

From these expressions we can obtain the amount of energy required to displace the electrons from the orbit n to the orbit n'.

In the actual experiments the gas or vapour is bombarded by the electrons emitted by a glowing filament, the motions of the electrons being accelerated by an adjustable electric field. The energy of these electrons is obtained from the expression

$$eV = mv^2/2,$$

where V is the potential difference and v is the velocity. Assuming that the electron gives up to the atom the whole of its energy on collision, we may substitute the energy difference required, $W_n - W_{n'}$, by eV,

whence
$$V = \frac{vhN}{e}\left[\frac{1}{(n + \mu_1)^2} - \frac{1}{(n' + \mu_2)^2}\right]$$

or
$$V = \frac{N}{8102}\left[\frac{1}{(n + \mu_1)^2} - \frac{1}{(n' + \mu_2)^2}\right] \quad . \quad . \quad (10)$$

since $vh/e = 300 \times 3 \times 10^{10} \times 6{\cdot}545 \times 10^{-27}/4{\cdot}774 \times 10^{-10}$ volts. It is very convenient to express the energy in terms of volts, since in the actual experiments the potential difference through which the emitted electrons pass is measured. The above expression (10) gives us the relation between the wave-number of the line emitted when the electron falls from orbit n' to orbit n and the voltage necessary to supply the energy required to produce the reverse process, namely, the displacement of the electron from orbit n to orbit n'. If $1/\lambda$ is the wave-number of the radiation emitted during the return of

the electron, the voltage necessary to displace the electron will be $1/8102\lambda$.

It is evident that two phenomena will be observed when gaseous atoms are subjected to bombardment by external electrons. In the first case the atomic electron may be shifted from its normal orbit n to another orbit n', in which case the radiation will be observed of a single line caused by the return of the displaced electron to orbit n. The voltage potential necessary to produce this electron shift is known as a resonance or radiation potential. In the second case the atomic electron may be removed altogether and the atom thereby ionised. The voltage potential necessary to carry this change into effect is known as the ionisation potential. In the former case the resonance potential will be given by $1/8102\lambda$, where $1/\lambda$ is the wave-number of the radiation emitted by the atomic electron falling back into its normal orbit. In the latter case the ionisation potential will be given by $1/8102\lambda_\infty$, where $1/\lambda_\infty$ is the limit of the series or the wave-number when $n' = \infty$.

This may be illustrated by the case of sodium and, since we know the readiness with which this element absorbs radiation of the same wave-numbers as the principal series, we may expect that the electron displaced by bombardment will be the one normally existing in the 1σ or innermost orbit and that it will be displaced either to the 1π orbit or to infinity (see Fig. 3, p. 69). We know that the radiation emitted by the return of the electron from the 1π orbit to the 1σ orbit has the mean wave-number 16969 and therefore the voltage potential necessary to supply the energy increment required to displace the electron from the 1σ orbit to the 1π orbit will be $16969/8102 = 2{\cdot}08$ volts. The displacement of the electron to infinity or the ionisation of the sodium atom will require $41449/8102 = 5{\cdot}12$ volts, since the limit of the principal series $= 1\sigma = 41449$. The voltage values observed by Tate and Foote[1] were 2·12 and 5·12, respectively. Another example may be given, namely, that of mercury, in which no effect occurs on bombardment until the voltage potential reaches 4·76, at which value radiation commences. Increase in the potential fall produces no further change until 6·45 volts is reached, when suddenly the radiation is increased. Then again, no further increase in the radiation occurs until the voltage is increased to 10·2 when the atoms become ionised.[2] Now the ionisation potential of 10·2 volts corresponds to $n_\infty = 8102 \times 10{\cdot}2 = 826404$, and this is obviously the limit of the principal series of singlets for which 1S has been calculated to be 84178·5. This suggests that the electron is most readily displaced from the 1S orbit and that the two resonance potentials are due to the displacement of the electron from this orbit to two other orbits. It seems that this is what actually happens, since the wave-number of the first line of the principal series of singlets

[1] *Phil. Mag.*, **36**, 64 (1918).
[2] Mohler, Foote, and Meggers, *Journ. Opt. Soc.*, Amer., **4**, 364 (1920).

is 54065·7 ($\lambda = 1849{\cdot}57$), and there is a very strong line at $\lambda = 2536{\cdot}52$, the wave-number of which is 39412·6 given by the combination $1S - 1p_2 = 84178{\cdot}5 - 44768{\cdot}9 = 39409{\cdot}6$, where $1p_2$ is the central orbit of the principal series of triplets. The values of the voltages calculated from the three values of n are 4·86, 6·67, and 10·38 compared with the observed values of 4·76, 6·45, and 10·2 respectively.

An analogous case is that of calcium, for which Mohler, Foote, and Stimson [1] have found two resonance potentials of 1·90 and 2·85 volts and the ionisation potential of 6·01 volts. Here again it is the innermost orbit from which the electron is displaced, namely, the orbit 1S, which is the limit of the principal series of singlets. The orbit 1S has the wave-number 49304·8 and the first line of the series has the wave-number 23652·4, whilst the wave-number of the combination $1S - 1p = 15210{\cdot}3$. The calculated voltages corresponding to these electron shifts are 1·89, 2·92, and 6·08 respectively.

The elements sodium, mercury, and calcium exist as free atoms in the vapour state, and the question arises as to the resonance and ionisation potentials of molecules consisting of more than one atom. Such cases are not free from difficulty as may be instanced by the resonance and ionisation potentials of hydrogen, which are 10·5 and 16·9 volts respectively.[2] The wave-number of the line given by the fall of the electron from orbit 2 to orbit 1 (see Fig. 2, p. 68) is $N/1^2 - N/2^2 = 82258$ and hence the resonance potential should be $82258/8102 = 10{\cdot}15$, which is in very fair agreement with the observed value. On the other hand, the ionisation potential should be $109678{\cdot}3/8102 = 13{\cdot}53$, which is materially less than the observed value of 16·9. If we consider the extra energy necessary to dissociate the hydrogen molecule into atoms, this can easily be arrived at from the heat of dissociation of hydrogen which is known to be 84000 calories per gram molecule.[3] If we take one calorie as $4{\cdot}174 \times 10^7$ ergs and the number of molecules in a gram molecule as $6{\cdot}22 \times 10^{23}$, the energy required to dissociate a single hydrogen molecule into neutral atoms will be

$$8{\cdot}4 \times 10^4 \times 4{\cdot}174 \times 10^7/6{\cdot}22 \times 10^{23} = 5{\cdot}64 \times 10^{-12} \text{ ergs} = w,$$

and the corresponding dissociation potential will be

$$300w/e = 300 \times 5{\cdot}64 \times 10^{-12}/4{\cdot}774 \times 10^{-10} = 3{\cdot}54 \text{ volts}.$$

Adding this to the calculated value of the ionisation potential we have $13{\cdot}53 + 3{\cdot}54 = 17{\cdot}07$ volts, which is very near the observed value of 16·9 volts.

There is some difficulty in reconciling the fact that ionisation does not take place until the total energy necessary to dissociate the molecules and ionise the resulting atoms has been supplied with the fact that the observed resonance potential is the same as the

[1] *Phil. Mag.*, **40**, 73 (1920).
[2] Horton and Davies, *Proc. Roy. Soc.*, A, **97**, 23 (1920).
[3] Langmuir, *J. Amer. Chem. Soc.*, **37**, 451 (1915).

theoretical value for hydrogen atoms within the limit of experimental error. Why is it possible to obtain the resonance of hydrogen atoms without also supplying the energy necessary to dissociate the molecules into atoms? By analogy with the ionisation potential measurements the first resonance potential should be found at $10{\cdot}5 + 3{\cdot}54 = 14{\cdot}04$ volts, and no neutral atom should be present to respond to the observed value of 10·5 volts. As a matter of fact, although radiation is observed at 10·5 volts, there is a considerable increase when the voltage is increased to 13·9, and consequently it would seem that there must be present some neutral atoms in the gas owing to some other cause. Hicks [1] suggests that, since the resonance potential is about three times the dissociation potential, a single bombarding electron at 10·5 volts is capable of dissociating three hydrogen molecules and that there are formed in this way sufficient neutral atoms to show radiation at this voltage. On the other hand, Compton and Olmstead [2] suggest that a certain amount of dissociation is caused by the action of the hot filament used as the source of electrons.

The values obtained for oxygen and nitrogen [3] are capable of being explained on the same lines, but helium and the other rare gases present a problem of considerable interest since they are known to be monatomic. According to Bohr [4] the total energy of the neutral helium atom is 6·13 times that of hydrogen and the potential difference corresponding to the amount of energy necessary to remove both electrons will be $13{\cdot}53 \times 6{\cdot}13 = 82{\cdot}94$ volts. Since, as has already been shown, the value of N in the enhanced series of helium is four times that for hydrogen, it follows that the voltage potential required to remove the second electron to infinity from singly ionised helium will be $13{\cdot}53 \times 4 = 54{\cdot}12$ volts. The energy required for the first ionisation, therefore, will correspond to the voltage potential of $82{\cdot}94 - 54{\cdot}12 = 28{\cdot}8$ volts. Compton and Lilly [5] find that the ordinary series of helium lines are excited at about 25·5 volts and the enhanced line series at about 80 volts, provided that the bombarding electron stream is not too dense.

The agreement between calculation and observation is eminently satisfactory, particularly in respect of the value of 54·5 volts for the second ionising potential. There is, however, considerable difficulty in interpreting the very high value for the first ionising potential of 25·5 volts, which corresponds to a wave-number of $25{\cdot}5 \times 8102 = 206601$. It is obvious that no atom can give "arc" series of lines with a greater limit than 109768·3 which is the value of N for these series, since in any formula for spectral series the variable term is always less than unity. The maximum ionisation potential, neglecting the extra energy required for dissociation, is shown by hydrogen and is 13·53 volts. The problem is intensified in interest

[1] *Analysis of Spectra*, p. 117. Cambridge University Press, 1922.
[2] *Phys. Rev.*, **17**, 45 (1921).
[3] Mohler, *Bull. Bur. Standards*, **16**, 669 (1921).
[4] *Phil. Mag.*, **26**, 489 (1913).
[5] *Astrophys. Journ.*, **52**, 1 (1920).

by the fact that in helium no radiation is induced with moderately dense electron streams below 25·5 volts and that at this voltage lines of the various arc series are emitted. The following lines were observed by Compton and Lilly at 30 volts, $\lambda = 7066$, 6678, 5876, 5048, 5016, 4922, 4713, 4472, 4438, and 4388. These lines are distributed amongst five series and the largest limit is that of the principal series of singlets, to which $\lambda = 5016$ belongs, namely, 32032·5. The voltage corresponding to this series limit is 32032·5/8102 = 3·96 volts. The suggestion may be made that, in spite of the fact that helium is monatomic, work must be done on the system before the atoms can respond in the expected way to bombardment by external electrons. A possible explanation of the necessity for the preliminary work was put forward from another point of view [1] and Hicks [2] has more recently made a somewhat similar suggestion. Mention may also be made of the fact that the voltage potentials of argon and neon are abnormally high compared with the values calculated from their spectral series.

It is important to note in this connection that the monatomic vapours of the alkali metals exhibit as an absorption spectrum the lines of the principal series, it being a matter of history that the laboratory experiment of obtaining the reversal of the D lines of sodium lead Kirchhoff to the enunciation of the law known under his name. It is thus obvious that the atoms of these elements are in a position at once to respond to the vibration characteristic of their principal series without the necessity of any previous supply of energy, this being independent of the fact that the observed and calculated values of the ionisation potential agree in each case. The two sets of observations are thus in agreement and together afford conclusive evidence that the excess of the observed values over the calculated values with certain elements is due to the fact that work must be done on the normal molecules before the atoms are obtained in the state in which they can respond to the vibrations characteristic of their spectral series. Since the amount of this work can easily be calculated we are able to determine the loss of energy suffered by the free atoms when they settle down to the molecular conditions in which they normally exist in the free state.

The calculation given above for hydrogen shows that when the necessary data are to hand it is possible to calculate the value of the additional energy and thus quantitatively explain the discrepancy between the observed and calculated ionisation potentials of the elements. The whole of the phenomena described in this section, therefore, afford a striking support to the Bohr theory of the atom as applied to spectral series.

Enhanced Line Series. The existence of enhanced lines, that is to say, spectrum lines, the intensity of which is enhanced in passing from the conditions obtaining in the arc to those in the spark, has

[1] Baly, *Phil. Mag.*, **40**, 18 (1920). [2] *Analysis of Spectra*, p. 118.

already been referred to in Vol. II., Chap. II., p. 132. The importance of these lines is particularly great in connection with astronomical spectroscopy in view of their presence in the spectra of many stars. Lockyer attributed these lines to the higher temperature conditions prevalent in the spark, and under the belief that a type of atomic disintegration had been induced he gave the prefix of "proto" to the substance so formed. Thus the enhanced lines of calcium and magnesium were assigned to protocalcium and protomagnesium respectively.

The enunciation of the Bohr theory of spectral lines has led to a new interpretation of the origin of enhanced lines, and indeed the fact that these lines form series which conform to Bohr's general formula has added a very fascinating chapter to the history of the modern development of atomic spectroscopy. For the first and pioneer work in this particular field we are indebted to Fowler who was able definitely to prove the reality of series of enhanced lines. This advance has since been consolidated and considerably extended by Fowler, Paschen, Millikan, and many others.

The opening of this new chapter arose over the so-called Pickering series of hydrogen lines described on p. 18 and Rydberg's expression of these as the diffuse series of hydrogen. Rydberg also calculated from the two series the so-called principal series of hydrogen, the first member of which has $\lambda = 4686$ and has been recognised in the spectra of several stars and nebulæ. This interpretation of the origin of these lines was universally accepted, the close analogy of their series formulæ with that of the Balmer series being a justification, in spite of the fact that no one had succeeded in producing the new lines from hydrogen in the laboratory. In 1912 Fowler [1] found by passing strong condensed discharges through helium, containing hydrogen as an impurity, that the Pickering series of lines showed faintly, together with the lines which Rydberg had attributed to the principal series of hydrogen. This 4686 series also contained other lines which could be expressed as a second principal series of hydrogen, closely related to the first.

When Bohr enunciated his theory it was clear that no hydrogen lines could exist beyond those expressed by the general formula [2]

$$\nu = \mathrm{N}\left(\frac{1}{n^2} - \frac{1}{n'^2}\right),$$

and he suggested that the lines in question were due to ionised helium, that is to say the atom of helium which has lost one electron. He showed that the general formula in this case would be

$$\nu = 4\mathrm{N}\left(\frac{1}{n^2} - \frac{1}{n'^2}\right).$$

[1] *Roy. Ast. Soc.*, M.N., **73**, 62 (1912).

[2] From now onwards the usual convention will be adopted by using the symbol ν to denote both wave-numbers and oscillation frequencies. Except where specifically stated to the contrary, wave-numbers will be employed.

Since the phenomena are due to a single electron and a nucleus with charge twice that on the electron, the analogy between these series of lines and the authentic hydrogen lines is thus explained, since the only difference between He^+ and H lies in the factor $2^2 = 4$ present in the formula for the former.

The investigation of the problem thus raised was undertaken by Fowler,[1] who recognised that the lines in question must be regarded as enhanced lines, the ionisation of the helium atom being caused by the condensed spark discharge, and he made a general investigation of the lines of this class. The problem involved was to determine whether the enhanced lines of any element could be expressed by series formulæ containing the factor 4N in place of N which is characteristic of the series formulæ for arc lines.

Fowler first of all investigated magnesium, which, as is well known, exhibits the strong enhanced line $\lambda = 4481$ and, since it was known that this line is a close doublet, this was a valuable indication of the type of series to which it belongs. The enhanced magnesium lines given in Table XXXI. were found to agree with the 4481 line in that they are close doublets with constant wave-number difference. Only in the case of the first three lines could the wave-lengths of both components be measured.

TABLE XXXI.

λ in I.A.	Δλ.	ν in vacuo.	Δν.
4481·327	0·198	22308·68	0·99
4481·129		22309·67	
3104·805	0·092	32198·99	0·94
3104·713		32199·93	
2660·821	0·066	37571·43	0·94
2660·755		37572·37	
2449·573		40811·31	
2329·58		42913·30	
2253·87		44354·65	
2202·68		45385·36	
2166·28		46147·66	

In order to represent the series by a formula, only one of the components was used, namely, the less refrangible. The last five lines

[1] *Phil. Trans.*, A, **214**, 225 (1914).

may be regarded as consisting of two components separated by $\Delta\nu = 0{\cdot}99$, and since the more refrangible component has about double the intensity of the less refrangible, the wave-numbers of the two components may be regarded as the wave-number of the unresolved line $+ 0{\cdot}33$ and $- 0{\cdot}66$ respectively. The whole series of the less refrangible components can be expressed by a formula containing 4N, there being insufficient accuracy to decide which is best—the Rydberg, Hicks, or Ritz formula. Since, however, it appears that the Hicks formula is the best in general, the results given by the formula

$$\nu = 49775{\cdot}20 - \frac{4 \times 109679{\cdot}3}{(n + 0{\cdot}994541 + 0{\cdot}006170/n)^2}$$

only need be given, and they are set fourth in Table XXXII.

TABLE XXXII.

ν.	n.	Limit of error.	Error of calculation.
22308·68	3	0·02	0·00
32198·99	4	0·05	0·00
37571·43	5	0·14	0·00
40810·65	6	0·17	+ 0·21
42912·64	7	0·4	+ 0·25
44353·99	8	1·0	+ 0·70
45384·70	9	1·0	+ 0·86
46147·24	10	1·1	+ 1·00

The first three lines were used in the calculation of the constants.

Fowler next discusses the enhanced lines of calcium and strontium which consist in each case of two series of wide doublets and narrow doublets, respectively, and he shows that the wave-numbers (on Rowland's scale) of the four series can be well expressed by the Hicks formula with the constant 4×109675. He further shows that the two magnesium doublets measured by him in conjunction with Payn [1] are the first two members of two other series, the wave-numbers of which on the International scale can again be expressed by Hicks's formulæ with $4 \times 109679{\cdot}3$. In addition to these, two combination series conforming to the same type were discovered in magnesium.

As regards the relations between these series Fowler states the following. The fundamental series in the doublet systems of calcium, strontium, and barium derives its limit and the separation of its components from an observed negative term of the diffuse series. In the case of magnesium, the corresponding negative term of the diffuse series together with the derived fundamental series is absent. A new group of series of narrow doublets (often called the F.P. system)

[1] *Proc. Roy. Soc.*, A, **72**, 255 (1903).

exists in magnesium, in which the separation of the sharp and diffuse doublets is identical with the calculated separation of the second pair of the principal series of wider doublets. This group includes two combination series, seven lines in each having been observed. The 4481 series of magnesium consists of very close doublets with constant wave-number difference, and this forms the fundamental series of the F.P. system. Its limits are derived from the first negative term of the diffuse series.

The general nature of the series formula for these enhanced lines having been proved to conform to Bohr's theory, Fowler next investigated the Pickering series and the 4686 series attributed to hydrogen. He shows that the latter can be expressed by the formula

$$\nu = 4 \times 109719{\cdot}78\left(\frac{1}{3^2} - \frac{1}{n^2}\right)$$

whereas on Rydberg's explanation the alternate lines belonged to two series having a simple relation to one another. Clearly therefore this series is of the enhanced type and this is supported by the fact that it has been found by Evans [1] that the spark discharge in pure helium excites these lines. As the result of this it is natural to expect that the Pickering series is of the same type, and Fowler shows that, as first suggested by Bohr, these lines can be expressed by the formula

$$\nu = 4 \times 109719{\cdot}78\left(\frac{1}{4^2} - \frac{1}{n^2}\right).$$

The fact that both series can each be expressed by one formula affords strong evidence that they both are enhanced helium lines and, further, we have the fact, as shown on p. 66, that the ratio of $4N_{He}$ to N_H is almost identical with that calculated by Bohr. There can be no doubt therefore that Bohr's predictions were experimentally verified by Fowler within a remarkable degree of accuracy.

One important fact should be noted in connection with the enhanced lines of helium, namely, their general similarity to hydrogen. This is obvious from the close analogy between the He^+ and the H formulæ. Thus the enhanced formula for the Pickering lines may be written

$$\nu = 109719{\cdot}78\left(\frac{2^2}{4^2} - \frac{2^2}{n^2}\right)$$
$$= 109719{\cdot}78\left(\frac{1}{2^2} - \frac{2^2}{n^2}\right),$$

and consequently every alternate line will have very nearly the same wave-number as a line of the Balmer series of hydrogen. In fact the values will be identical if the value of N were the same for the two elements. It is not surprising therefore that Rydberg was

[1] *Phil. Mag.*, **29**, 284 (1915).

led to believe that both series, Balmer and Pickering, were due to hydrogen.

In the same paper Fowler pointed out that although, on Bohr's theory, series of still more enhanced lines due to doubly and even trebly ionised atoms with formulæ involving $N \times 3^2$ and $N \times 4^2$ are to be expected, he himself at that time had not been able to obtain any evidence of their existence. During the following years the existence of other enhanced line series (4N) was demonstrated, but it was not until recently that the enhanced series of the type 9N, 16N, etc., were discovered.

Almost simultaneously in 1923 were published two papers, one by Paschen [1] describing the spectrum of Al^{++} with series constant 9N, and the second by Fowler [2] in which he describes the spectrum of Si^{+++} with series constant of 16N.

Before this later work is described mention may be made of the law of spectroscopic displacement, enunciated by Kossel and Sommerfeld,[3] which is analogous to the well-known law of radioactivity. Whereas the latter law states that in a radioactive change accompanied by the loss of an α-particle or helium atom the element produced belongs to that sub-group in the periodic table which is next but one to the sub-group to which the radioactive parent belongs, the spectroscopic displacement law deals with spectroscopic analogies when atoms are ionised. This law states that the enhanced spectrum of a singly ionised element is analogous in structure to the arc spectrum of the element preceding it in the periodic table. We have already seen this law evidenced in the close analogy between the enhanced spectrum of helium and the ordinary line spectrum of hydrogen. Further evidence of this law was given by Reinheimmer [4] who showed the qualitative analogy between the spark spectrum of rubidium and the ordinary spectrum of krypton. Again, Zeeman and Dik [5] showed a relationship between the spark spectrum of potassium and the ordinary spectrum of argon. The more recent evidence will be discussed later.

As is known the arc spectra of the alkali metals show doublet systems, whilst the second, third, and fourth groups show triplet, doublet, and triplet systems respectively.[6] According to the Kossel and Sommerfeld law the enhanced series of the second group when singly ionised should show doublet systems analogous to those of the alkali metals. As already stated Fowler found that this was the case, and it is interesting to note that as pointed out by Kossel and Sommerfeld the separations of the doublets of the enhanced spectra of the second group are not very far removed from four times the separations

[1] *Ann. der Phys.*, **71**, 142 (1923).
[2] *Proc. Roy. Soc.*, **103**, 413 (1923).
[3] *Deutsch. phys. Ges., Verh.*, **21**, 240 (1919).
[4] *Ann. der Phys.*, **71**, 162 (1923). [5] *Ibid.*, 199 (1923).
[6] This statement is to be modified in the sense foreshadowed on p. 38, and more fully developed below on p. 135.

of the arc doublets in the corresponding alkali metals, which shows the close analogy since we have 4N in the enhanced series.

The law also applies to the higher stages of ionisation of aluminium and silicon. Thus the arc spectrum of aluminium consists of doublet systems, but the enhanced spectrum of Al^{+} consists of triplets [1] analogous to the arc spectrum of magnesium, whilst the enhanced spectrum of Al^{++} consists of doublets analogous to the arc spectrum of sodium. Similarly, the spectra of Si, Si^{+}, Si^{++}, Si^{+++}, consist of triplets, doublets, triplets, and doublets respectively, the last again being analogous to the arc spectrum of sodium.

This law is of great importance and renders considerable aid to the investigator in his search for series systems in enhanced line spectra. It must not be forgotten, however, in the comparison of an enhanced spectrum with an arc spectrum, that the separation intervals in the former are greater owing to the presence of 4N, 9N, 16N, in the series formula. There is another result which ensues from the large value of the series constant, namely, the general displacement towards the ultra-violet. This means that the higher members of the series lie in the Schumann region and therefore their detection and measurement involve the special difficulties of work in that region.[2]

We may now return to Paschen's discovery of the spectrum of Al^{+++} and Fowler's discovery of the spectrum of Si^{+++}. In passing it may be noted that there are two methods of nomenclature adopted for the different stages of ionisation. Hitherto the system of denoting the number of electrons lost has been used, but Paschen used the Roman numerals I., II., III., IV., etc., to denote the neutral atom, the singly, doubly, and trebly ionised atom, respectively. For example, the symbols Al^{++} and Al III. mean the same thing, as also do the symbols Si^{+++} and Si IV. The Paschen symbols have been generally adopted.

In the case of doubly ionised aluminium, Paschen was able to measure a considerable number of lines and he showed that they all could be arranged in a doublet system, the series formulæ of which all involved the term 9N, the value of N being 109735·0. The lines extended from $\lambda = 5722$ to $\lambda = 1353$.

Fowler's investigation of the spectrum of Si IV. may be described in some detail, for it forms a typical instance of the work involved in an investigation in a hitherto unknown region of spectral series, complicated by the fact that the majority of the lines have very small wave-lengths. It may be stated at the commencement that this work formed one section of a complete investigation of the silicon series, which are of peculiar interest from the point of view of astrophysics. The difficulties, therefore, were not lessened by the fact that the Si IV. lines had to be recognised amongst whole systems of lines belonging to Si II. and Si III. At the same time from the Kossel and Sommerfeld law Fowler was able to assume at

[1] *Ann. der Phys.*, **71**, 537 (1923).

[2] See below, p. 262.

the outset that the series system of Si IV. would consist of doublets, analogous to those of Na I., and on Bohr's theory he also assumed in the first instance that the series constant would have the value of 16N, namely 1754852. Subsequently, we may deal with his work on the spectra of Si II. and Si III.

Owing to the large value of the Rydberg constant the Si IV. series corresponding to the best-known series of Na I. lie in the extreme ultra-violet, whilst those lines of Si IV. which lie in the ordinary region correspond to the secondary series of Na I. in the infra-red, which have only been partially observed. Further, the intensities in any one series decrease rapidly with increase in order number, so that the number of lines available for calculation of the constants are somewhat restricted. Fowler then proceeds as follows:—

Taking the stronger components of the secondary pairs, which have a separation of $\Delta\nu = 162$, he obtains with the use of the Rydberg formula in the first instance

$$\left.\begin{aligned}\sigma_1(2) &= 2\pi_1 - 2\sigma = -24450\\ \sigma_1(3) &= 2\pi_1 - 3\sigma = \ \ 46989\end{aligned}\right\}\sigma_1(m) = 146112 - \frac{16N}{(m + 1{\cdot}207606)^2}$$

$$\left.\begin{aligned}\delta_1(2) &= 2\pi_1 - 2\delta = -58050\\ \delta_1(3) &= 2\pi_1 - 3\delta = \ \ 31579\end{aligned}\right\}\delta_1(m) = 144374 - \frac{16N}{(m + 0{\cdot}944363)^2},$$

the negative sign being used because two of the pairs have their stronger components on the more refrangible side. The limits for the sharp and diffuse series are as close as could be expected from the simple Rydberg formula, and this may be taken as provisional evidence in favour of the value 16N.

Since the formula for the sharp series is as a general rule more exact, it is justifiable to calculate from it the value of the term 1σ, and derive an approximate formula for the associated principal series. We have from the above

$$1\sigma = \frac{16N}{(2{\cdot}207606)^2} = 360082,$$

$$2\pi_1 = 146112 = \frac{16N}{(3{\cdot}465606)^2},$$

$$2\pi_2 = 146112 + 162 = \frac{16N}{(3{\cdot}463687)^2},$$

and hence

$$\pi_1(m) = 1\sigma - m\pi_1 = 360082 - \frac{16N}{(m + 1{\cdot}465606)^2},$$

$$\pi_2(m) = 1\sigma - m\pi_2 = 360082 - \frac{16N}{(m + 1{\cdot}463687)^2}.$$

The first principal pair will thus have the wave-numbers 71415 and 70965, respectively, with $\Delta\nu = 450$. Since Millikan, Bowen, and Sawyer [1] have observed two silicon lines with $\lambda = 1402{\cdot}9$ and $1393{\cdot}9$

[1] *Astrophys. Journ.*, **53**, 159 (1921).

or $\nu = 71280$ and 71740 ($\Delta\nu = 460$), these may be accepted as the leading pair of the first principal series.

The possibility of lines belonging to the fundamental series was next considered and, since the knowledge gained from other spectra leads to the view that the corresponding terms are rather larger than $N(m + 1)^2$, it is probable that $3\phi > 16N/4^2$, say 110000, and that $4\phi > 16N/5^2$, say 71000. The limit may be either 2δ or 3δ, which may be found from

$$2\delta = 2\pi_1 - \delta_1(2) = 146112 + 58050 = 204162,$$
$$3\delta = 2\pi_1 - \delta_1(3) = 146112 - 31579 = 114533,$$

and hence

$$2\delta - 3\phi = 204162 - 110000 = 94162,$$
$$3\delta - 4\phi = 114533 - 71000 = 43533.$$

There is little doubt that the line measured by Simeon [1] at $\lambda = 1066{\cdot}3$, $\nu = 93782$, is the first line, and Fowler observed a line at $\lambda = 2287{\cdot}08$, $\nu = 43710$, which corresponds with the second.

Although the above would seem to justify the applicability of the series formulæ with 16N, further evidence is afforded by an independent calculation of the constant from the data for the $\sigma\pi$ lines. Thus

$$\nu_1 = \frac{B}{(1+s)^2} - \frac{B}{(1+p)^2} = 71740,$$
$$\nu_2 = \frac{B}{(2+s)^2} - \frac{B}{(2+p)^2} = 24450,$$
$$\nu_3 = \frac{B}{(3+s)^2} - \frac{B}{(2+p)^2} = -46989.$$

The value of B was calculated to be $15{\cdot}846N$ which is nearer to 16N than could have been expected and, as the result of the accumulated evidence, 16N was used in all the subsequent calculations.

The most probable values of the series terms may now be calculated from the best available data, namely,

$$1\pi_1 - 1\sigma = -71740,$$
$$2\pi_1 - 2\sigma = -24450,$$
$$2\pi_1 - 3\sigma = 46989,$$
$$2\pi_1 - 2\delta = -58050,$$
$$2\pi_1 - 3\delta = 31579,$$
$$3\pi_1 - 3\delta = -26571.$$

$$2\delta - 3\phi = 93782,$$
$$3\delta - 4\phi = 43710,$$
$$3\delta - 5\phi = 65212,$$
$$4\delta - 5\phi = 23732,$$
$$4\delta - 6\phi = 36702,$$

The ϕ terms appear to be the most suitable for the calculation on account of their greater number, and by various combinations the following values for their consecutive differences are found :—

$$3\phi - 4\phi = 39557,$$
$$4\phi - 5\phi = 21502,$$
$$5\phi - 6\phi = 12970.$$

[1] *Proc. Roy. Soc.*, **102**, A, 490 (1923).

By the method of least squares we obtain the formula

$$m\phi = \frac{16N}{(m + 0{\cdot}988903 + 0{\cdot}019900/m)^2},$$

the use of the Hicks formula being now justified by the greater accuracy. From this we find $3\phi = 109923{\cdot}4$, $4\phi = 70366{\cdot}3$, $5\phi = 48861{\cdot}7$, and $6\phi = 35893{\cdot}1$. These in turn lead to values for the δ terms, and thence to the π_1 and σ terms, thus

$$2\delta = 109923 + 93782 = 203705.$$

From the $2\pi_1$, $3\pi_1$ terms and the 2σ, 3σ terms the following formulæ have been derived :—

$$m\pi_1 = \frac{16N}{(m + 1{\cdot}492563 - 0{\cdot}043080/m)^2},$$

$$m\sigma = \frac{16N}{(m + 1{\cdot}228166 - 0{\cdot}032538/m)^2}.$$

Extrapolations give $1\pi_1 = 292477$, and $1\sigma = 364018$. The difference is 71541, which is as close to the observed line 71740 as can be expected. As there is no reason to suppose that one of the terms is more correct than the other, one has been increased and the other diminished by an equal amount, so as to make the difference equal to the wave-number of the line to which it corresponds. Thus the adopted values are $1\sigma = 364117$, $1\pi_1 = 292377$.

For the calculation of additional terms of the diffuse series the following formula was derived from the 3δ and 4δ terms :—

$$m\delta = \frac{16N}{(m + 0{\cdot}900071 + 0{\cdot}066204/m)^2}.$$

Extrapolation gives $2\delta = 203969$ which is in close agreement with the value 203705 derived above.

Finally, the first three π_2 terms have been derived by adding the observed separations of the corresponding pairs to the respective π_1 terms. The $2\pi_2$ and $3\pi_2$ values then give the following formula for the calculation of the additional π_2 terms :—

$$m\pi_2 = \frac{16N}{(m + 1{\cdot}490667 - 0{\cdot}043146/m)^2}.$$

In this way the four types of series, sharp, principal, diffuse, and fundamental, have been recognised and their constants determined. The definite realisation now gained of the constant 16N has rendered possible the recognition of types of series which previously escaped notice owing to their occurrence in the infra-red. Amongst such series there was recognised one by Fowler in the case of Mg II., namely, $3\phi - m\phi$, but the agreement between observation and calculation was outside the limits of experimental error and for this reason it was omitted from the account of Fowler's first work on enhanced series

given above. Since that paper was published Bohr has extended his theory and has shown that his general theory leads to a fifth series of quantum states for which ϕ' differs but little from ϕ in the fundamental series. As the result of this Bohr finds that the errors inherent in Fowler's series of Mg II., $3\phi - m\phi$, disappear if $m\phi'$ is substituted for $m\phi$. Series of this type, differing slightly from the ordinary fundamental series, were found by Paschen in Al III. and Fowler has identified a similar series in Si IV. Yet another series, $4\phi' - m\phi''$, was detected by Fowler in Si IV. and also noted by Paschen in Al III. Owing the smallness of the wave-lengths, both these series in Si IV. were only recognised as far as their earliest members.[1]

Fowler gives the values of the various series terms which he has evaluated in the case of Si IV. and these may be quoted, together with the complete table he gives of the Si IV. lines apportioned to their series. In Tables XXXIII. and XXXIV. the Rydberg numeration of the terms is given in brackets, together with the Bohr total quantum[2] numbers. As Fowler points out the latter are more correct, but the former more readily facilitate comparison with previously existing series data.

In Table XXXIV. the terms which have not been observed are enclosed in brackets.

The Kossel and Sommerfeld law suggests a comparison between the separation intervals which occur in the spectra that should be comparable, namely, the spectra of Si IV., Al III., Mg II., and Na I. As has already been shown the separations of doublets or triplets, observed in any group of the periodic table, increase with the atomic weight, but no direct relation has been observed. On the other hand, in the case of the four spectra now under consideration in which the value of E/e is 4, 3, 2, and 1, respectively, a regularity is to be found. Since the value of the series constant N in the four spectra is proportional to $(E/e)^2$, we may plot the values of $\Delta\nu$ against 16, 9, 4, and 1. This was done by Paschen for the last three spectra, but as the result of Fowler's work all four spectra may be compared. Fowler shows that the points obtained lie nearly on a straight line, but there is a definite curvature which can be expressed by the formula

$$\Delta\nu = 7{\cdot}5 + 36{\cdot}9(x^2 - 0{\cdot}492),$$

where $x = E/e$. This is the closest relation yet discovered and it affords a good confirmation of the Kossel and Sommerfeld law. Another method is to compare together the series constants for the corresponding terms in the four spectra and this was done by Fowler. In order to make the comparison demanded by the Kossel and Sommerfeld law the actual terms for Na I., Mg II., Al III., Si IV., have been divided by 1^2, 2^2, 3^2, 4^2, respectively. In view of the fact that Paschen used the value 109735 for the series constant, Fowler re-calculated the values for Al III. with N_H as the constant in order

[1] See also below, p. 289.

[2] See below, p. 107.

TABLE XXXIII.

SERIES OF Si IV.

1st Principal. $3(1)\sigma - m\pi$.
$3(1)\sigma = 364117$.

λ in I.A.	ν.	Δν.	B.	m. R.	$m\pi_{1,2}$.
1393·9 (10)	71740	460	3	(1)	292377
1402·9 (8)	71280				292837
(457·75)	218462	162	4	(2)	145655
(458·09)	218300				145817

1st Sharp. $3(1)\pi - m\sigma$.
$3(1)\pi_1 = 292377$; $3(1)\pi_2 = 292837$.

λ in I.A.	ν.	Δν.	B.	m. R.	$m\sigma$.
— 1393·9 (10)	71740	460	3	(1)	364117
— 1402·9 (8)	71280				
(817·85)	(122272)	460	4	(2)	170105
(814·78)	(122732)				

1st Diffuse. $3(1)\pi - m\delta$.
$3(1)\pi_1 = 292377$; $3(1)\pi_2 = 292837$.

λ in I.A.	ν.	Δν.	B.	m. R.	$m\delta$.
(1127·75)	(88672)	460	3	(2)	203705
(1121·93)	(89132)				
(560·85)	(178301)	460	4	(3)	114076
(559·41)	(178761)				

2nd Principal. $4(2)\sigma - m\pi$.
$4(2)\sigma = 170105$.

λ in I.A.	ν.	Δν.	B.	m. R.	$m\pi_{1,2}$.
4088·863 (10)	24449·80	162·10	4	(2)	145655
4116·104 (8)	24287·99				145817
(1210·65)	(82600)	75	5	(3)	87505
(1211·75)	(82525)				87580
(859·25)	(111708)	41	6	(4)	(58397)
(859·52)	(111667)				(58438)

2nd Sharp. $4(2)\pi - m\sigma$.
$4(2)\pi_1 = 145655$; $4(2)\pi_2 = 145817$.

λ in I.A.	ν.	Δν.	B.	m. R.	$m\sigma$.
— 4088·863 (10)	— 24449·80	162·10	4	(2)	170105
— 4116·104 (8)	— 24287·99				
2127·48 (4)	46989·05	161·57	5	(3)	98666
2120·19 (3)	47150·62				
(1230·71)	81254	162	6	(4)	64401
(1228·26)	81416				

2nd Diffuse. $4(2)\pi - m\delta$.
$4(2)\pi_1 = 145655$; $4(2)\pi_2 = 145817$.

λ in I.A.	ν.	Δν.	B.	m. R.	$m\delta$.
— 1722·7 (5)	— 58050	162	3	(2)	203705
— 1727·4 (4)	— 57888				
3165·72 (8)	31579·28	162·02	4	(3)	114076
3149·56 (6)	31741·30				
(1368·72)	(73061)	162	5	(4)	72594
(1365·69)	(73223)				

1st Fundamental. $3(2)\delta - m\phi$.
$3(2)\delta = 203705$.

λ in I.A.	ν.	B. m. R.	$m\phi$.
1066·3 (8)	93782	4 (3)	109923
(749·97)	(133339)	5 (4)	70366

2nd Fundamental. $4(3)\delta - m\phi$.
$4(3)\delta = 114076$.

λ in I.A.	ν.		B. m. R.	$m\phi$.
2287·08	43710·37		5 (4)	70366
1533·47	65212	—	6 (5)	48862
(1279·05)	(78183)	—	7 (6)	35893

3rd Fundamental. $5(4)\delta - m\phi$.
$5(4)\delta = 72594$.

λ in I.A.	ν.	B. m. R.	$m\phi$.
4212·44 (3)	23732·43	6 (5)	48862
2723·82 (1)	36702·30	7 (6)	35892

Series $5(4)\phi - m\phi'$.
$5(4)\phi = 70366$.

λ in I.A.	ν.	B. m. R.	$m\phi'$.
4631·38 (3*n*)	21585·80	6 (5)	48780
2895·13 (1)	34530·67	7 (6)	35835

Series $4(3)\phi - m\phi'$.
$4(3)\phi = 109923$.

λ in I.A.	ν.	B. m. R.	$m\phi'$.
2517·52 (5)	39709·67	5 (4)	70213

Series $5(4)\phi' - m\phi''$.
$5(4)\phi' = 70213$.

λ in I.A.	ν.	B. m. R.	$m\phi''$.
4654·14 (4*n*)	21480·25	6 (5)	48733

Combinations.

λ in I.A.	ν.	ν calculated.
3762·41 (4)	26571·18	$4(3)\delta - 5(3)\pi_1 = 26571$
3773·13 (3)	26495·69	$4(3)\delta - 5(3)\pi_2 = 26496$
1796·1 (1)	55676	$4(3)\delta - 6(4)\pi_1 = 55679$
1797·5 (0)	55633	$4(3)\delta - 6(4)\pi_2 = 55638$

TABLE XXXIV.

THE SERIES TERMS OF Si IV.

Rydberg Numbers.	σ.	π_1.	π_2.	δ.	ϕ.	ϕ'.	ϕ''.	Bohr Numbers.
(1)	364117	292377	292837					3
(2)	170105	145655	145817	203705				4
(3)	98666	87505	87580	114076	109923			5
(4)	(64401)	(58397)	(58438)	72594	70366	70213		6
(5)	(45319)	(41741)	(41766)	(50186)	48862	48788	48733	7
(6)	(33638)	(31319)	(31335)	(36741)	35893	35835	(35800)	8
				(28050)	(27476)			

to bring them into line with his own values for the others. The values are given in Table XXXV.

TABLE XXXV.

COMPARISON OF SERIES TERMS.

Bohr numbers . . .		3.	4.	5.	6.	7.
Rydberg numbers . .		(1).	(2).	(3).	(4).	(5).
$m\sigma$	Na I.	41449·0	15709·5	8248·3	5077·3	3437·3
	Mg II.	30316·9	12865·5	7120·3	4517·3	3120·7
	Al III.	25493·3	11475·2	6533·7	(4216)	—
	Si IV.	22757·3	10631·6	6166·6	(4025)	—
$m\pi_1$	Na I.	24475·7	11176·1	6406·3	4151·3	—
	Mg II.	21376·6	10154·0	5949·6	3909·2	—
	Al III.	19502·4	9525·3	5663·3	(3756)	—
	Si IV.	18273·6	9103·4	(5469)	(3650)	—
Rydberg numbers . .		(2).	(3).	(4).	(5).	(6).
$m\delta$	Na I.	12276·2	6900·4	4412·5	3061·9	2248·6
	Mg II.	12444·2	6988·8	4461·6	3091·6	2267·4
	Al III.	12609·4	7072·7	4507·1	3118·4	2284·3
	Si IV.	12731·6	7129·8	4537·1	(3137)	(2296)
$m\phi$	Na I.	—	6860·4	4390·4	(3042)	—
	Mg II.	—	6866·9	4394·3	3051·2	2241·4
	Al III.	—	6869·7	4396·6	3052·2	2242·1
	Si IV.	—	6870·2	4397·9	3053·9	2243·3

As can be seen the σ and π terms diminish, whilst the δ and ϕ terms increase in passing from Na I. to Si IV. When the corresponding first sharp, principal, or diffuse terms are plotted against the atomic

numbers, the points lie on smooth curves, so that the regularity is much greater than appears in a similar comparison of terms of the elements of the same groups of the periodic table.

In order to maintain continuity we may next take up Fowler's later work on the spectra of Si II. and Si III., as well as that of Si I. In order fully to understand the meaning of some of the observations and the arguments used by him, a knowledge of the more recent developments of Bohr's theory is necessary. These extensions of the theory will be discussed in the following sections, and if a historical sequence were maintained these should have had first place. On the other hand, Fowler's work on the spectra of silicon affords such an admirable example of pioneer work that it has seemed preferable to describe it as a whole.

The investigation of the spectra of silicon was carried considerably further by Fowler by his recognition of the series systems of Si I., Si II., and Si III.[1] The arc spectrum Si I. contains altogether about 78 lines, of which only 13 occur in the visible spectrum and only 4 in the region between $\lambda = 3900$ and $\lambda = 2640$, the remainder being found between $\lambda = 2640$ and $\lambda = 1841$. The complete series arrangement of these lines has not as yet been traced, but it is evident that the system is based on singlet and triplet terms, as indeed would be expected from the position of silicon in the periodic table. The triplet series, however, is but weakly represented, and as the first members occur far in the ultra-violet, succeeding members would only be expected as weak lines in the Schumann region.

A triplet of the sharp and another of the diffuse series are unmistakable. These are given in Table XXXVI.

TABLE XXXVI.

Sharp triplet.			Diffuse triplet.		
λ in I.A.	ν.	$\Delta\nu$.	λ in I.A.	ν.	$\Delta\nu$.
2452·136 (3)	40768·42		2218·917 (1)	45052·96	
		146·12			17·00
2443·378 (3)	40914·54		2218·080 (2)	45069·96	
		77·10			28·36
2438·782 (3)	40991·64		2216·165 (4)	45098·32	
					146·03
			2211·750 (2)	45198·92	
					17·15
			2210·912 (3)	45216·07	
					77·17
			2207·980 (2)	45276·09	

[1] *Phil. Trans.*, **225**, 1 (1925).

No definite evidence has been found of the existence of other triplets, but three lines, in an isolated group of five, show the same intervals—

λ in I.A.	ν.	Δν.
1880·71 (1)	53171	
		147
1875·54 (2)	53318	
		76
1872·87 (2)	53394	

The first line, which in a regular series would be the strongest, is, however, definitely the weakest, and it is possible that the occurrence of the two intervals is accidental.

Some of the most intense lines of the arc spectrum are included in the well-known group of six lines at $\lambda = 2528$ to $\lambda = 2506$, all of which are reversed in the arc. These form a pp^* multiplet,[1] involving the two separations noted above, and it follows that the first terms of the combinations which give rise to the lines must be $1p_1$, $1p_2$, and $1p_3$. The scheme of this multiplet is

p_1.		p_2.		p_3.	
		39605·89 (8)			$p_3{}^*$
		77·14			
39537·01 (9)	146·02	39683·03 (7)	77·01	39760·04 (7)	$p_2{}^*$
194·72		194·80			
39731·73 (10)	146·10	39877·83 (9)			$p_1{}^*$

A second multiplet of the same type occurs at $\lambda = 1989$ to $\lambda = 1978$, and the detailed structure is as follows :—

p_1.		p_2.		p_3.	
50277·3 (4R)	146·3	50423·6 (3)			$p_1{}^{**}$
66·8		67·2			
50344·1 (2)	146·7	50490·8 (2)	77·1	50567·9 (3)	$p_2{}^{**}$
		35·9			
		50526·7 (2)			$p_3{}^{**}$

The wave-numbers in this group are subject to a little uncertainty of measurement, but it is evident that there are involved the regular p terms and a second asterisk term p^{**}, which it will be noted is a reversed term.

All the terms entering into the above multiplets clearly belong to the triplet system. No multiplets involving quintet terms have as yet

[1] The existence of " multiplets " has not been mentioned up to the present in this chapter. They were first discovered by Catalan in 1922, and this great advance will be dealt with on p. 119 *et seq*. It is necessary to mention these instances here together with the occurrence of " asterisk " terms, in order not to break the continuity in describing Fowler's work on the four spectra of silicon. The same remark applies to the " reversed " p^{**} term, which enters into the second multiplet, as well as to certain quantum numbers ; these will be dealt with in the following sections.

been observed. Although the actual values of the various p terms cannot be calculated, their differences can be found with considerable accuracy. In particular the difference $1p_2^* - 1s$ may be noted.

$1p_1 - 1s = 40768{\cdot}42$
$1p_1 - 1p_2^* = 39537{\cdot}01$
therefore $1p_2^* - 1s = 1231{\cdot}41$

$1p_2 - 1s = 40914{\cdot}54$
$1p_2 - 1p_2^* = 39683{\cdot}03$
therefore $1p_2^* - 1s = 1231{\cdot}51$

$1p_3 - 1s = 40991{\cdot}64$
$1p_3 - 1p_2^* = 39760{\cdot}04$
therefore $1p_2^* - 1s = 1231{\cdot}60$

Mean 1231·51

In the singlet system of Si I., there are six lines which are reversed in the arc and which apparently belong to the sharp and diffuse series. A fourth line of the sharp series is suggested by the greater intensity of the more refrangible component of a pair of Si II. lines, $\lambda = 1817$ and $\lambda = 1808$, which appears in the spectrum of the silicon spark in hydrogen with large self-induction. This line is near the expected position of the fourth member of the sharp series and Fowler regards it as such.

Sharp Series of Singlets.

λ in I A.		ν.
2881·585	(10R)	34692·97
2124·140	(6R)	47062·94
1901·00	(5R)	52603·9
1808·14		55305

The formula calculated from the last three lines for $1P - mS$ is

$$\nu = 60072 - \frac{N}{\left(m + 0{\cdot}689685 + \frac{0{\cdot}427838}{m}\right)^2}$$

Diffuse Series of Singlets.

2435·159	(8R)	41052·61
2058·20	(5R)	48570·51
1893·02	(2R)	52832

$$\nu = 59339{\cdot}0 - \frac{N}{\left(m + 0{\cdot}933784 + \frac{0{\cdot}515257}{m}\right)^2}$$

The correcting terms are unusually large, and the two values of 1P differ more than usual, but as the sharp series is generally more accurate than the diffuse, the value is adopted of

$$1P = 60072.$$

With this limit, the terms and "effective quantum numbers" $(\sqrt{N/\text{term}})$ are given in Table XXXVII.

TABLE XXXVII.

Terms.	$\sqrt{N/\text{term}}$.	Terms.	$\sqrt{N/\text{term}}$.
1S = 25379·03	2·078837	1D = 19019·39	2·401387
2S = 13009·06	2·903604	2D = 11502·49	3·087909
3S = 7468·1	3·832263	3D = 7240·2	3·892110
4S = 4767	4·796648		

The increase in the successive values of the effective quantum number departs much more from unity than is usual in most of the known series, but the fact that the seven lines are readily reversed is strongly in favour of the above arrangement.

Fowler draws attention to the remarkable occurrence of the separation 1231·51($1p_2^* - 1s$) in connection with some of the strong singlets, including the first member of the sharp series. Thus

$$25597{\cdot}61\ (9) - 24365{\cdot}89\ (5) = 1231{\cdot}72$$
$$34692{\cdot}97\ (10) - 33461{\cdot}39\ (5) = 1231{\cdot}58$$

Then again, combinations between triplet and singlet terms are suggested by the following lines :—

$$\left.\begin{array}{l} 17645{\cdot}64\ (1) - 17568{\cdot}52\ (2) = 77{\cdot}12 \\ 17707{\cdot}97\ (2) - 17513{\cdot}19\ (5) = 194{\cdot}78 \\ 33656{\cdot}27\ (1) - 33461{\cdot}39\ (5) = 194{\cdot}88 \end{array}\right\} = 1p_3 - 1p_2 = 1p_3^* - 1p_2^*$$
$$= 1p_2^* - 1p_1^*$$

We may next consider the spectrum of the singly ionised silicon atom which consists of a doublet system. In this case the value of the Rydberg constant has to be multiplied by 4, and in the following the value of 4N has been taken as 438713·2. The two series $1\pi - m\sigma$ and $2\pi - m\sigma$ are distinguished as the first and second sharp series, the same distinction being used for the two diffuse series. As in the case of the arc spectrum of aluminium the Si II. spectrum does not contain the term 1σ.

In the principal series there are three pairs which serve for the calculation of the series limit. The stronger components are as follows :—

$$2\sigma - 2\pi_1 = 15750{\cdot}90$$
$$2\sigma - 3\pi_1 = 38384{\cdot}52$$
$$2\sigma - 4\pi_1 = 48562{\cdot}70$$

and the formula is

$$\nu = 66297{\cdot}06 - \frac{4N}{\left(m + 1{\cdot}001375 - \frac{0{\cdot}110567}{m}\right)^2}.$$

The $2\pi_1$ term is thus 50546·16 and the $2\pi_2$ term is 50606·16, since the separation is $\Delta\nu = 60$.

The limits of the second sharp and diffuse series should of course be equal to $2\pi_1$ and $2\pi_2$, and the values of these limits calculated from the two series should agree with those already found.

Second Sharp Series.

$$\left.\begin{aligned} 2\pi_2 - 3\sigma &= 16780{\cdot}61 \\ 2\pi_2 - 4\sigma &= 29992{\cdot}96 \\ 2\pi_2 - 5\sigma &= 36772{\cdot}91 \end{aligned}\right\} \nu = 50621{\cdot}40 - \frac{4N}{\left(m + 0{\cdot}644962 - \frac{0{\cdot}133206}{m}\right)^2}.$$

Second Diffuse Series.

$$\left.\begin{aligned} 2\pi_2 - 3\delta_2 &= 19831{\cdot}58 \\ 2\pi_2 - 4\delta_2 &= 31203{\cdot}07 \\ 2\pi_2 - 5\delta_2 &= 37330{\cdot}50 \end{aligned}\right\} \nu = 50710{\cdot}77 - \frac{4N}{\left(m + 0{\cdot}661311 + \frac{0{\cdot}323876}{m}\right)^2}.$$

If a Ritz formula be employed of the type

$$\nu = A - \frac{4N}{[m + \mu + \alpha(A - \nu)]^2}$$

the values of the limits are found to be 50638·13 and 50683·24, respectively. The four values agree with one another and with the value 50606·16 as well as can be expected.

The fundamental series contains narrow doublets with $\Delta\nu = 16{\cdot}6$ which is equal to that of the chief line and satellite in the first diffuse doublet. The more refrangible components may be given, together with the derived formula (Hicks).

Fundamental Series.

$$\left.\begin{aligned} 2\delta_2 - 3\phi &= 24217{\cdot}69 \\ 2\delta_2 - 4\phi &= 34421{\cdot}75 \\ 2\delta_2 - 5\phi &= 39972{\cdot}60 \end{aligned}\right\} \nu = 52483{\cdot}11 - \frac{4N}{\left(m + 0{\cdot}894930 + \frac{0{\cdot}134295}{m}\right)^2}.$$

From this we have $2\delta_2 = 52483{\cdot}11$, $2\delta_1 = 52466{\cdot}51$, and $3\phi = 28265{\cdot}42$. Owing to the fact that the first diffuse doublet lies in the far infra-red it is not possible to compare these values with the terms for the other series. With the help of the value of 3ϕ and

certain combination series we can adjust all the limits and also find the value of 1π.

There is a group of three spark lines at $\lambda = 3862$ which has the appearance of an inverted diffuse doublet and therefore must have negative wave-numbers assigned to it. These cannot be deduced from any of the already known terms, but may be represented by introducing new terms of diffuse type, x_1 and x_2. These terms combine with the ϕ terms to give a strong series of fundamental type in the extreme ultra-violet, commencing with a pair at $\lambda = 2073$. In order to obtain greater consistency of numerical results, Fowler adjusts the wave-numbers of this pair so as to make their separation 15·91, like that of the two more accurately measured lines $\nu = 25942$ and 25926, to which they are related. The observed wave-numbers 48232·89 and 48248·49 were altered to 48232·74 and 48248·65. The two terms x_1 and x_2 may be calculated as follows :—

$$\begin{aligned} x_1 - 3\phi &= 48232{\cdot}74 \\ 3\phi &= 28265{\cdot}42 \end{aligned} \qquad \begin{aligned} x_2 - 3\phi &= 48248{\cdot}65 \\ 3\phi &= 28265{\cdot}42 \end{aligned}$$

Therefore $x_1 = 76498{\cdot}16$ and $x_2 = 76514{\cdot}07$.

We then have

$$\begin{aligned} 2\pi_1 - x_2 &= -25942{\cdot}05 \\ & \qquad\qquad 2\pi_1 = 50572{\cdot}02 \\ 2\pi_1 - x_1 &= -25926{\cdot}14 \\ & \qquad\qquad 2\pi_2 = 50632{\cdot}03 \\ 2\pi_2 - x_2 &= -25882{\cdot}04 \end{aligned}$$

These values of $2\pi_1$ and $2\pi_2$ are very close to those calculated previously and may be used to fix the common limits of the second sharp and diffuse series. The term 2σ can at once be derived.

$$\begin{aligned} 2\sigma - 2\pi_1 &= 15750{\cdot}90 \\ 2\pi_1 &= 50572{\cdot}02 \\ \text{therefore} \quad 2\sigma &= 66322{\cdot}92 \end{aligned}$$

Lastly, we have the first sharp and diffuse series which lie in the extreme ultra-violet. The first member of the sharp series is at $\lambda = 1533$, whilst the first member of the diffuse series is at $\lambda = 1265$. Fowler calculated the common limits of the two series from the sharp pair $1\pi - 2\sigma$ by means of the value of 2σ given above.

$$\left.\begin{aligned} 1\pi_1 - 2\sigma &= 65208 \\ 1\pi_2 - 2\sigma &= 65495 \end{aligned}\right\} \begin{aligned} 1\pi_1 &= 131531 \\ 1\pi_2 &= 131818 \end{aligned}$$

In this way all the limits required have been determined. The complete system of Si II. lines so far as they have been observed are given in Table XXXVIII.

TABLE XXXVIII.

FIRST SHARP SERIES. $1\pi - m\sigma$; $1\pi_1 = 131531$; $1\pi_2 = 131818$.

λ, Intensity.	ν.	Δν.	m(+2).	mσ.
1533·55 (10) 1526·83 (8)	65208 65549	287	(2)	66323
(1023·75) (1020·75)	(97680) (97967)	(287)	(3)	33851
(901·78) (899·45)	(110892) (111179)	(287)	(4)	20639

PRINCIPAL SERIES. $2\sigma - m\pi$; $2\sigma = 66322{\cdot}92$.

λ, Intensity.	ν.	Δν.	m(+2).	$m\pi_1$, $m\pi_2$.
– 1533·55 (10) – 1526·83 (8)	– 65208 – 65495	287	(1)	131531 131818
6347·091 (10) 6371·359 (8)	15750·90 15690·90	60·00	(2)	50572·02 50632·02
2604·44 (2) 2606·09 (1)	38384·52 38360·21	24·31	(3)	27938·40 27962·71
2058·53 (1) 2058·92 (0)	48562·70 48553·61	9·09	(4)	17760·2 17769·3

SECOND SHARP SERIES. $2\pi - m\sigma$; $2\pi_1 = 50572{\cdot}02$; $2\pi_2 = 50632{\cdot}02$.

λ, Intensity.	ν.	Δν.	m(+2).	mσ.
– 6347·091 (10) – 6371·359 (8)	– 15750·90 – 15690·90	60·00	(2)	66322·92
5978·970 (5) 5957·612 (4)	16720·03 16780·61	59·98	(3)	33851·40
3339·84 (3) 3333·16 (2)	29932·98 29992·96	59·98	(4)	20639·05
2726·74 (2) 2722·29 (1)	36662·99 36722·91	59·92	(5)	13909·07

FIRST DIFFUSE SERIES. $1\pi - m\delta$; $1\pi_1 = 131531$; $1\pi_2 = 131818$.

λ, Intensity.	ν.	λcalc.	νcalc.	Δν.	m + (1).	$m\delta_2$, $m\delta_1$.
1265·04 (10)	79049	1265·06 1264·78	79048 79065	16·6		52483
1260·66 (8)	79324	1260·48	79335	287	(2)	52466
993·09 (1) 990·32 (1)	100696 100977	992·74 989·92	100731 101018	287	(3)	30800

SECOND DIFFUSE SERIES. $2\pi - m\delta$; $2\pi_1 = 50572{\cdot}02$; $2\pi_2 = 50632{\cdot}02$.

λ, Intensity.	ν.	Δν.		m(+ 1).	$m\delta_2$, $m\delta_1$.
Out of range	(− 1911·09) (− 1894·49) (− 1851·09)	(16·60)	(60·00)	(2)	52483·11 52466·51
5056·353 (2) 5055·975 (7) 5041·020 (5)	19771·60 19772·90 19831·58	1·30	59·98	(3)	30800·42 30799·12
3210·04 (3) 3203·89 (2)	31143·30 31203·07		59·77	(4)	19428·8
2682·27 (2) 2677·98 (1)	37270·80 37330·50		59·70	(5)	13301·4

FUNDAMENTAL SERIES. $2\delta - m\phi$; $2\delta_1 = 52466{\cdot}51$; $2\delta_2 = 52483{\cdot}11$.

λ, Intensity.	ν.	Δν.	m(+ 1).	mφ.
4130·884 (10) 4128·053 (8)	24201·08 24217·69	16·61	(3)	28265·42
2905·70 (3) 2904·29 (2)	34405·06 34421·75	16·69	(4)	18061·40
2501·99 (1) 2500·96 (1)	39956·15 39972·60	16·45	(5)	12510·43

COMBINATION SERIES OF Si II. $x - m\phi$; $x_1 = 76498{\cdot}16$; $x_2 = 76514{\cdot}07$.

λ, Intensity.	ν.	Δν.	Calculated.
— 3853·657 (3)	— 25942·05	15·91*	$2\pi_1 - x_2$
— 3856·021 (8)	— 25926·14	60·01	$2\pi_1 - x_1$ } Used for calculation of $2\pi_1$, $2\pi_2$
— 3862·592 (6)	— 25882·04		$2\pi_2 - x_2$
2072·61 (10)	48232·89	15·60	$x_1 - 3\phi$
2071·94 (8)	48248·49		$x_2 - 3\phi$ } Used for calculation of x_1, x_2
1817·06 (10)	55034	271	$1\pi_1 - x_2 = 55017$, $\lambda = 1817{\cdot}62$.
1808·14 (8)	55305		$1\pi_1 - x_1 = 55033$, $\lambda = 1817{\cdot}09$.
			$1\pi_2 - x_2 = 55304$, $\lambda = 1808{\cdot}19$.
1711·0 (6*d* ?)	58445	—	$x_1 - 4\phi = 58437$, $\lambda = 1711{\cdot}2$.
			$x_2 - 4\phi = 58453$, $\lambda = 1710{\cdot}8$.
1563·1 (3*d* ?)	63975	—	$x_1 - 5\phi = 63988$, $\lambda = 1562{\cdot}8$.
			$x_2 - 5\phi = 64004$, $\lambda = 1562{\cdot}4$.
1485·4 (3)	67322	—	$x_1 - 6\phi = 67329$, $\lambda = 1485{\cdot}2$.
			$x_2 - 6\phi = 67345$, $\lambda = 1484{\cdot}9$.
1438·9 (1*n*)	69498	—	$x_1 - 7\phi = 69494$, $\lambda = 1439{\cdot}0$.
			$x_2 - 7\phi = 69510$, $\lambda = 1438{\cdot}6$.
1408·8 (0*n*)	70982	—	$x_1 - 8\phi = 70974$, $\lambda = 1409{\cdot}0$.
			$x_2 - 8\phi = 70990$, $\lambda = 1408{\cdot}6$.

* This is definitely smaller than the separation in the fundamental series (16·61).

The largest Si II. term is a *p* term which has the azimuthal quantum number 2. On the new Bohr theory, to be discussed later, it appears therefore that the thirteenth electron moves in a 3_2 orbit. The second ionisation potential of silicon deduced from the value of $1\pi_2$, is 16·27 volts.

In accordance with the Kossel and Sommerfeld law of spectroscopic displacement, the series of Si II. should be similar to those of Al I. Both systems consist of doublets and differ chiefly in the wider separation of the doublets in Si II., and in the displacement of lines of Si II. to a region of much shorter wave-length as compared with the corresponding lines of Al I. This is due to the greater charge on the atomic trunk acting on the 13th electron in Si II. as compared with that of Al I. Thus the near ultra-violet lines of Al I. are represented by Si II. lines in the Schumann region, whilst the infra-red lines of Al I. correspond with visible lines of Si II. The main doublet separations, $1\pi_2 - 1\pi_1$, are 112 for Al I. and 287 for Si II., the ratio being 1 : 2·56.

The effective quantum numbers are compared together in Table XXXIX.

TABLE XXXIX.

Bohr numbers		3.	4.	5.	6.	7.
$m\sigma$	Al I.	—	2·186892	3·217954	4·227570	5·231357
	Si II.	—	2·571925	3·599996	4·610472	5·616184
$m\pi_2$	Al I.	1·507207	2·674639	3·700549	4·709045	—
	Si II.	1·824328	2·943593	3·960963	4·968841	—
$m\pi_1$	Al I.	1·508958	2·675967	3·701923	4·710388	—
	Si II.	1·826318	2·945339	3·962685	4·970115	—
$m\delta_1$	Al I.	2·631031	3·425462	4·260130	5·164510	—
	Si II.	2·891673	3·774168	4·751900	5·743038	—
$m\phi$	Al I.	—	3·968941	4·963713	—	—
	Si II.	—	3·939695	4·928499	5·921808	—

It is to be noted that the strong Si II. series, $x - 3\phi$, has not as yet been found in Al I.

The spectrum of ionised carbon C II. was analysed by Fowler,[1] and he compares the systems of C II. and Si II. This comparison is of considerable interest as it is known that elements of the same sub-group of the Periodic Table exhibits certain progressive spectral differences with increase in atomic number.

In the first place, the main doublet separations of C II. and Si II. are 58 and 287, respectively, the ratio being 5·0, whereas the ratio of the squares of the atomic numbers, 6 and 14, is 5·4. The spectral terms are set forth in Table XL., and it may be seen that they conform to the general rule that the limits of the sharp and principal series (1π and 2σ) are displaced towards the red with increase in the atomic number. On the other hand, the δ and ϕ terms increase with increase in atomic number, which is also the case with the alkali metals. Both the ionised elements have an x term, and Fowler lays stress on the fact that this term is definitely of δ type in Si II. and apparently of σ type in C II.

We may now consider the spectrum of Si III., which consists of triplets and singlets. One of the triplets, having its strongest line at $\lambda = 4552$, is well known in the spark spectrum and certain stellar spectra. Although a second triplet occurs with its strongest component at $\lambda = 3806$, the Si III. spectrum is not well obtained under ordinary spark conditions. These lines are best excited when the condensed discharge is passed through silicon tetrafluoride in vacuum tubes. As in the case of Si II. the chief members lie in the extreme ultra-violet and lines in the ordinary region of observation belong to secondary series.

[1] *Proc. Roy. Soc.*, **105**, 299 (1924).

TABLE XL.

Rydberg numbers		1.	2.	3.	4.	5.
x	C II.	—	100165	—	—	—
x_2	Si II.	—	76514	—	—	—
$m\sigma$	C II.	—	80121	39425	23311	(15387)
	Si II.	—	66323	33851	20639	13909
$m\pi_2$	C II.	196670	64934	34140	—	—
	Si II.	131818	50632	27963	17769	—
$m\delta$	C II.	—	51108	28535	18164	(12558)
	Si II.	—	52466	30800	19429	13301
$m\phi$	C II.	—	—	27680	17703	12283
	Si II.	—	—	28265	18061	12510

There is no need to give the details of Fowler's calculations of the series limits of the triplet system, for the method has already been sufficiently indicated. It may be noted that two of the four triplets observed in the ordinary range are inverted and must therefore be given negative signs in the calculation of the limits. One of these, with its strongest line at $\lambda = 3806$, is accompanied by satellites and these are abnormal as they appear on the more refrangible (actually less refrangible on account of the inversion) side of the chief lines. It follows that the d term is an inverted term, *i.e.*, $d_1 > d_2 > d_3$, and the same was observed by Paschen in the corresponding triplet in Al II.

The triplet system, so far as it has been observed, is shown in Table XLI.

TABLE XLI.

First Sharp Series. $1p - ms$; $1p_1 = 216879$; $1p_2 = 217142$; $1p_3 = 217273$.

Observed.			Calculated.			$m(+2)$.	ms.
λ.	ν.	$\Delta\nu$.	λ.	ν.	$\Delta\nu$.		
997·70	100230	249	997·81	100219	263	(2)	116660
995·23	100479	—	995·20	100482	131		
—	—		993·91	100613			

FIRST DIFFUSE SERIES. $1p - md$; $1p_1 = 216879$; $1p_2 = 217142$; $1p_3 = 217273$.

Observed.			Calculated.	$m(+1)$.	md_1, d_2, d_3.
λ.	ν.	Δν.			
1113·76	89786	266	Used for calculation of $1p$.	(2)	127093
1110·47	90052	132			127091
1108·85	90184				127089

FUNDAMENTAL SERIES. $2d - mf$; $2d_1 = 127093{\cdot}00$; $2d_2 = 127090{\cdot}86$; $2d_3 = 127088{\cdot}85$.

Observed.			Calculated.			$m(+1)$.	mf_1, f_2, f_3.
λ.	ν.	Δν.	λ.	ν.	Comb.		
1500·39	66649	41	1500·39	66649·00	d_1f_1	(3)	60444·00 60483·44 60511·23
1501·32	66608		1501·29	66609·56	d_1f_2		
		30	1501·34	66607·42	d_2f_2		
1502·00	66578		1501·91	66581·77	d_1f_3		
			1501·96	66579·63	d_2f_3		
			1502·01	66577·62	d_3f_3		
1142·74 ?	87509	161			d_1f_1	(4)	39584 ? 39744 ?
1144·85 ?	87348				$d_{21}f_2$		

PRINCIPAL SERIES. $2s - mp$; $2s = 116659{\cdot}56$.

λ, Intensity.	ν.	Δν.	$m(+2)$.	mp_1, p_2, p_3.
— 997·70	— 100230	249	(1)	216890
— 995·23	— 100479	(134)		217139
—	— (100613)			217273
4552·654 (9)	21959·17	73·16	(2)	94700·39
4567·872 (7)	21886·01	33·02		94773·55
4574·777 (4)	21852·99			94806·57

SECOND SHARP SERIES. $2p - ms$; $2p_1 = 94700{\cdot}33$: $2p_2 = 94773{\cdot}54$; $2p_3 = 94806{\cdot}64$.

λ, Intensity.	ν.	Δν.	m(+ 2).	ms.
— 4552·654 (9)	— 21959·17			
— 4567·872 (7)	— 21886·01	73·16	(2)	116659·56
— 4574·777 (4)	— 21852·99	33·02		
3241·67 (6)	30839·43			
3234·00 (5)	30912·57	73·14	(3)	63861·01
3230·55 (3)	30945·58	33·01		

SECOND DIFFUSE SERIES. $2p - md$; $2p_1 = 94700{\cdot}33$; $2p_2 = 94773{\cdot}54$; $2p_3 = 94806{\cdot}64$.

λ, Intensity.	ν.	Δν.	m(+ 1).	md_1, d_2, d_3.
— 3086·225 (7)	— 32392·67			
— 3086·429 (3)	— 32390·53	2·14		
— 3086·620 (0)	— 32388·51	2·02		
		73·21	(2)	127093·00 127090·86 127088·85
— 3093·423 (6)	— 32317·31			
— 3093·613 (3)	— 32315·31	2·00		
— 3096·786 (4)	— 32282·21	33·10		
3806·56 (5)	26263·00			
3796·11 (4)	26335·30	72·30	(3)	68438·08
3791·41 (3)	26367·96	32·66		

$1S - 1p_2 = 39330$. $1S = 256472$.

SUPER-FUNDAMENTAL SERIES. $3f - mg$; $3f_1 = 60444{\cdot}00$; $3f_2 = 60483{\cdot}44$; $3f_3 = 60511{\cdot}23$.

λ, Intensity.	ν.	Δν.	m(+ 1).	mg.
4828·923 (4*n*)	20702·79			
4819·740 (3*n*)	20742·23	39·44	(4)	39741·21
4813·290 (2*n*)	20770·02	27·79		
3040·93 (1)	32875·14			
3037·26 (1)	32914·87	39·73	(5)	27568·82
3034·74 (1)	32942·20	27·33		

Six lines forming a pp^* multiplet may be arranged as follows :—

$1p_1$.		$1p_2$.		$1p_3$.	
(2)		(1)		(0)	i.
		76845			p_3^* (0)
		131			
76712	264	76976	133	77109	p_2^* (1)
264		263			
76976	263	77239			p_1^* (2)

$p_1^* = 139903$; $p_2^* = 140166$; $p_3^* = 140297$.

This group is well defined and confirms the main triplet separations given in Table XLI. A similar multiplet occurs in Al II. at $\lambda = 1767{\cdot}6$ and in Mg I. at $\lambda = 2783$.

The triplet separations of the three spectra, Mg I., Al II., and Si III. are compared in Table XLII. and as can be seen the ratio of the

TABLE XLII.

		Mg I.	Al II.	Si III.
At. wt.		24·32	27·1	28·3
Nuclear charge . .		12	13	14
Charge of core (c) . .		1	2	3
Separations	Δp_{21} . .	40·9	125·5	263
	Δp_{32} . .	19·9	61·8	131

two separations of the respective triplets is practically constant and equal to 2. Fowler also points out that there is a linear relation between the separation, and the square of the residual charges. Thus the equation

$$\Delta\nu = 13 + 28C^2$$

gives the values 41, 125, and 265. These separations, therefore, are much more simply related than those of successive elements belonging to the same sub-group. This was mentioned above in the case of the Si IV. spectrum. The values of the effective quantum numbers $\sqrt{9\mathrm{N}/\mathrm{term}}$, $\sqrt{4\mathrm{N}/\mathrm{term}}$, $\sqrt{\mathrm{N}/\mathrm{term}}$, for Si III., Al II., and Mg I., respectively, are given in Table XLIII.

As regards the singlet system of Si III. there are numerous lines which are excited simultaneously, or nearly so, with the Si III. triplets, and there is little doubt that many of these belong to the singlet system. Fowler, however, has not as yet succeeded in arranging these lines in series owing to want of information as to the lines in the region beyond $\lambda = 1200$. The resonance line, $1S - 1p_2$, and the first line of the principal series $1S - 1P$ have been identified with reasonable certainty.

TABLE XLIII.

Bohr numbers.		3.	4.	5.	6.
ms	Mg I.	—	2·314482	3·345514	—
	Al II.	—	2·691566	3·716978	—
	Si III.	—	2·908850	3·931549	—
mp_1	Mg I.	1·660865	2·817126	—	—
	Al II.	1·959816	3·075940	—	—
	Si III.	2·133402	3·228536	—	—
md_1	Mg I.	2·827920	3·829341	—	—
	Al II.	2·791874	3·801090	—	—
	Si III.	2·786896	3·797805	—	—
mf_1	Mg I.	—	3·959795	4·953992	—
	Al II.	—	3·928628	4·882470	
	Si III.	—	4·041150	4·993692 (?)	—
mg	Mg I.	—	—	—	—
	Al II.	—	—	4·982972	5·980675
	Si III.	—	—	4·983806	5·983737

Considerable assistance might be given by the singlet series of Mg I. and Al II., but the singlet system of the latter is not yet fully established. Paschen did not publish any singlet series, but an interesting attempt to identify these has been made by Russell,[1] who calculated the ratios of the corresponding *s*, *p*, and *d* terms of Al II. and Mg I., and plotted these against the known Mg I. terms. Then, from the S, P, and D terms of Mg I. the ratios of the singlet terms were found by interpolation. In this way rough values were found for the singlet terms of Al II. which suggested the allocation of some of the Al II. lines.

Fowler applies this method to the Si III. lines, but as only two members of each triplet series are known it can only be a question of linear interpolation or extrapolation. The data and results are given in Table XLIV.

TABLE XLIV.

	Al II.	Si III.	Ratio.		Al II.	Si III.	Ratio.
$2s$.	60589	116660	1·926	1S .	147107	(246200)	(1·674)
$1p_1$.	114281	216904	1·898	1P .	87262	(170600)	(1·954)
$2p_1$.	46393	94700	2·041	2P .	43759	(89580)	(2·046)

[1] *Nature*, **113**, 163 (1924).

The calculated ratios and singlet terms for Si III. are given in brackets. The value of 1S was obtained by a long extrapolation and may therefore be much in error. If the logarithms of the ratios are plotted against the logarithms of the terms there are obtained

$$1S = 267000, \quad 2S = 105600, \quad 1P = 169200, \quad 2P = 89740.$$

Fowler says that the most appropriate line for 1S — 1P in any reasonable accordance with the above is that at $\lambda = 1206{\cdot}9$, $\nu = 82857$. It is the strongest singlet in the range $\lambda = 1400$ to $\lambda = 990$ and so may be adopted with considerable confidence.

In order to identify the resonance line 1S — $1p_2$ we have $1p_2 = 217140$ and the two values of 1S given above. These give the wave-numbers

$$\nu = 29060$$
$$\nu = 49860.$$

Now the only singlets near this range are

λ.	ν.
3590	27844
3486	28670
2559	39063
2541	39330

There is every probability that the last line is due to the transition 1S — $1p_2$, since it is more strongly developed in the spark than any of the other lines, just as the resonance line of Al II. (Russell) makes its appearance in the arc, and that of Mg I. in the flame.

If the logarithms of the values of 1S — $1p_2$ be plotted against the logs of the $1p_2$ terms for Mg I., Al II., Si III., the value of 1S — $1p_2$ for Si III. is found to be $\nu = 41700$, which is in sufficient agreement with the adopted line $\nu = 39330$. The value of 1S — 1P is found to be $\nu = 83000$ which agrees almost exactly with the adopted line $\nu = 82857$.

If this identification be correct, we have the following :—

$$\begin{aligned} 1S - 1p_2 &= 39330 \\ 1p_2 &= 217142 \\ &= 256472 = 1S, \\ 1S - 1P &= 82857 \\ &= 173615 = 1P. \end{aligned}$$

Although plausible assignments of other singlet lines may be made, Fowler defers consideration of these until further data are available. The above values suggest that the resonance and ionisation potentials of Si III. are 4·85 and 31·66 volts respectively. Since the largest term is 1S, it may be concluded that the series electron in Si III. normally occupies a 3_1 orbit.

I have given this detailed account of Fowler's work on the spectra of silicon since it is a typical instance of pioneer work in a new field

of spectral series. As already noted in Vol. II., Chap. III., Fowler has solved the problem of the series architecture of several other enhanced line spectra, still retaining for the moment the old title. One of these, namely, the spectrum of O II. will be dealt with on p. 223 in connection with recent theories of complex spectra. Then again, a passing reference must be made to the remarkable investigations of Millikan and Bowen on the spectra given by their hot spark method in the very extreme ultra-violet. These spectra will be described in detail on p. 262. It is not possible to discuss them at the present stage since a knowledge of relativity principles is necessary to understand them and the methods used in their elucidation.

Sommerfeld's Extension of the Bohr Theory.—We may now consider a further extension of Bohr's theory which has led to very important and far-reaching results. The advance was due in the first instance to Sommerfeld, who succeeded in correlating many atomic phenomena in a most remarkable way by his development of the Bohr theory.[1] He first of all discussed the existence of elliptical orbits, the motion of the electron in an elliptical path, presenting a problem of two degrees of freedom, since its position is determined by two co-ordinates, namely, the azimuth ϕ and the radius vector q. Sommerfeld shows that the two quantum conditions for the system with two degrees of freedom are

$$\int_{\phi=0}^{\phi=2\pi} p_\phi d\phi = kh, \qquad \text{and} \qquad \int_{\phi=0}^{\phi=2\pi} p_q dq = rh \quad . \quad . \quad (1)$$

where p_ϕ and p_q are the impulse or momentum co-ordinates, and h is the Planck constant. The quantum number k may be called the azimuthal quantum number, whilst r may be called the radial quantum number.

By Kepler's second law p_ϕ is a constant during the motion and by putting $p = p_\phi$, the first equation in (1) becomes

$$\int_0^{2\pi} p_\phi d\phi = p \int_0^{2\pi} d\phi = 2\pi p = kh \quad . \quad . \quad . \quad (2)$$

From the second equation in (1) Sommerfeld, by re-stating it in terms of the orbital equation of the ellipse

$$\frac{1}{\gamma} = C_1 + C_2 \cos \phi,$$

shows that

$$\int_0^{2\pi} p_q dq = p\epsilon^2 \int_0^{2\pi} \frac{\sin^2 \phi}{(1 - \epsilon \cos \phi)^2} d\phi \quad . \quad . \quad . \quad (3)$$

[1] *Ann. der Phys.*, **51**, 1, 125 (1916); see also A. Sommerfeld, *Atombau und Spektrallinien*, 4te Auflage, p. 122. Vieweg und Sohn, Braunschweig, 1924.

where ϵ is the eccentricity. The integral can be transformed by partial integration to

$$\epsilon^2\int_0^{2\pi}\frac{\sin^2\phi d\phi}{(1+\epsilon\cos\phi)^2}=-\epsilon\int_0^{2\pi}\frac{\cos\phi d\phi}{1+\epsilon\cos\phi}=\int_0^{2\pi}\left(\frac{1}{1+\epsilon\cos\phi}-1\right)d\phi. \quad (4)$$

It can be proved that

$$\frac{1}{2\pi}\int_0^{2\pi}\frac{d\phi}{1+\epsilon\cos\phi}=\frac{1}{\sqrt{1-\epsilon^2}},$$

and consequently we obtain from (1)

$$\int_0^{2\pi}p_q dq = 2\pi p\left(\frac{1}{\sqrt{1-\epsilon^2}}-1\right)=rh. \quad . \quad . \quad (5)$$

Finally from (3) and (2) we have

$$\frac{1}{\sqrt{1-\epsilon^2}}-1=\frac{r}{k}$$

and

$$1-\epsilon^2=\frac{k^2}{(k+r)^2}=\frac{k^2}{n^2} \quad . \quad . \quad . \quad (6)$$

if we put the total quantum number n equal to the sum of the azimuthal and radial quantum numbers.

The constant p determines the size of the ellipse and the eccentricity ϵ determines its form. Hence by the azimuthal and radial quantum conditions given in (2) and (6) the size and form of the elliptical orbit are fixed in accordance with the quantum theory. As Sommerfeld says, there is thus selected from the continuous manifold of all possible ellipses a family of quantised ellipses given by the two quantum numbers k and r.

In his paper Sommerfeld draws attention to the fact that the foregoing quantum conditions were simultaneously and independently derived by H. A. Wilson.[1] Wilson, however, did not apply these equations to the Balmer series of lines.

Sommerfeld then calculates the energy and finds that

$$W=-\frac{2\pi^2me^2E^2}{h^2}\left[\frac{1}{(k+r)^2}\right]=-\frac{Nhx^2}{n^2} \quad . \quad . \quad (7)$$

where, as previously, x is the ratio of the charge on the nucleus to that on the electron. This is a most important result, for it shows that the energy of the elliptical orbits is the same as for circular orbits, with the one difference that the old quantum number is replaced by the sum of two quantum numbers $k + r$. Each of the

[1] *Phil. Mag.*, **31**, 161 (1916).

quantised ellipses therefore has an amount of energy equivalent to that of a definite Bohr circular orbit.

If we consider two ellipses of the family, one as the initial orbit with quantum numbers k and r, and another as the final orbit with quantum numbers k' and r', and calculate the energy emitted during the transition of an electron from the first to the second orbit, we have, on the Bohr frequency condition,

$$h\nu = \frac{2\pi^2 me^2 E^2}{h^2}\left[\frac{1}{(k+r)^2} - \frac{1}{(k'+r')^2}\right]$$

and

$$\nu = Nx^2\left[\frac{1}{(k+r)^2} - \frac{1}{(k'+r')^2}\right] \quad . \quad . \quad . \quad . \quad (8)$$

As can be seen by putting $x = 1$ this formula only gives the series of hydrogen lines and is indeed the Bohr formula with the quantum number n replaced by the sum of the azimuthal quantum number k and the radial quantum number r. The new formula has, however, a deepened theoretical significance and its origin has now multiple roots. By the admission of elliptical orbits the series has gained no extra lines and has lost none of its sharpness.

I have given Sommerfeld's treatment of the quantisation of plane elliptical orbits, since he was the first to derive the equations and to apply them to spectral series. In his original paper, to which reference has already been made, Bohr mentioned elliptical orbits, but based his theory of the radiation of discrete spectral lines on circular orbits. In later papers Bohr published his own method of quantisation, but this need not be given here. Reference may, however, be made to the defining of an elliptical orbit by the symbol n_k, where n is the total quantum number $(k + r)$ and k is the azimuthal quantum number.

The Quantum Theory of Series Systems.— The question now arises as to how the foregoing equations which involve the azimuthal and radial quantum numbers can be fitted into what we already know of the series systems. There is little difficulty in doing this as Sommerfeld has already shown, but, as will presently be seen, it is necessary to invoke a third quantum number in order to obtain a complete solution of the problem. The simplest possible condition exists, of course, in the hydrogen atom, which only shows one series of lines, known as the Balmer series. As we have already seen the quantisation of the Kepler ellipse leads to the same values of the energy and hence to the same spectrum lines as the quantisation of the circular orbit. It follows, therefore, that in the hydrogen spectrum the series terms will depend on the total quantum number and not on the azimuthal and radial quantum numbers separately. The same will be true of all the atoms of this type, such as the ionised helium atom He^+, the doubly ionised lithium atom Li^{++}, etc.

The case is different with all atoms which are not of the hydrogen type, since the pure Coulomb field no longer exists. We now find

that the series terms depend on the azimuthal and radial quantum numbers separately. In short, we may write the expression for the spectrum lines given by any atom which is not of the hydrogen type in the form

$$\nu = \phi(k, r) - \phi(k'r') \quad . \quad . \quad . \quad . \quad (9)$$

where each series term is some function of the azimuthal and radial quantum numbers. The reason for the divergence from the hydrogen type is, as Sommerfeld says,[1] that the external electron, thrown out of its normal orbit by some agency into an outer orbit, moves in the field of the nucleus which is screened off by the inner electron. A supplementary field is thereby introduced with the result that the orbits of the external electron are no longer Kepler ellipses.

In passing, it may be noted that Sommerfeld [2] has calculated three varyingly approximate expressions for the function $\phi(k, r)$. As a first approximation the atomic field may be regarded as a Coulomb field, that is to say, its potential energy with respect to the external electron is

$$\mathrm{E} = -\frac{e^2}{\gamma}.$$

We have then, as in the case of hydrogen,

$$\phi(k, r) = \frac{\mathrm{N}}{(k + r)^2} \quad . \quad . \quad . \quad (10)$$

For a second degree of approximation we may represent the potential energy of the atomic field by

$$\mathrm{E} = -\frac{e^2}{\gamma}\left(1 - \frac{c_1}{\gamma}\right)$$

when we obtain

$$\phi(k, r) = \frac{\mathrm{N}}{(k + r + \mu)^2} \quad . \quad . \quad . \quad (11)$$

where μ is a quantity which depends both on the constant c_1 of the atomic field and on the azimuthal quantum number. Since μ is independent of r, it forms a specific constant of a series.

For a third approximation the potential energy of the atomic field may be represented by

$$\mathrm{E} = -\frac{e^2}{\gamma}\left(1 - \frac{c_1}{\gamma} - \frac{c_2}{\gamma^2}\right)$$

when we obtain

$$\phi(k, r) = \frac{\mathrm{N}}{[k + r + \mu + \mu'\phi(k, r)]^2} \quad . \quad . \quad (12)$$

[1] *Atombau und Spektrallinien*, p. 493.
[2] *Sitzungsber. Akad.*, München (1916), 131.

where μ and μ' are dependent on k and the atomic field, but independent of r.

Now we know that the total quantum number n is the sum of the azimuthal and radial quantum numbers, and consequently we may write the expression (10) for the series term in the form

$$\frac{N}{n^2} \quad . \quad . \quad . \quad . \quad . \quad (10a)$$

which is the well-known Balmer term. Similarly in the case of the second approximation (11) we may write the expression for the series term in the form

$$\frac{N}{(n+\mu)^2} \quad . \quad . \quad . \quad . \quad (11a)$$

where μ is characteristic of the series. This of course is Rydberg's value for the series term. Lastly, the third approximation can be written in the form

$$\frac{N}{[n+\mu+\mu'(n,\mu,\mu')]^2} \quad . \quad . \quad . \quad (12a)$$

which is the Ritz form of the series term. As Sommerfeld says, "it is highly remarkable and satisfactory that the three types of spectral formulæ (Balmer, Rydberg, Ritz) which have been evolved slowly and laboriously, at widely different times, from the data of observation arrive naturally and simultaneously from our calculation."

Turning once again to equation (9) it may very readily be seen how the hitherto separate series are to be fitted into the general quantum scheme. This equation at once explains the resolution of the single Balmer series into a system of series, when the atoms are not of the hydrogen type. If we vary r' and keep k', k, and r constant, a single series of lines will be obtained, and if k' also varies a system of series will be obtained.

In the principal series the total quantum number assumes the values 2, 3, 4, etc., the general expression being

$$1s - mp, \quad \text{where } m = 2, 3, 4, \text{ etc.}$$

Since the lines in any one single series are given by integral variations in the radial quantum number only, Sommerfeld assumes that the lines of any single series are given by $r = 0, 1, 2$, etc. He concludes, therefore, that the principal series is always characterised by the azimuthal quantum number 2.

Similarly, since the diffuse series is expressed by

$$2p - md, \quad \text{where } m = 3, 4, 5, \text{ etc.},$$

he assumes that the diffuse series is characterised by the azimuthal quantum number 3. For the same reason he states that the characteristic azimuthal quantum number of the fundamental series is 4, and lastly he attributes to the sharp series the characteristic azimuthal quantum number 1.

It is interesting to note that as the azimuthal quantum number increases the difference between the spectral terms and those of the hydrogen type diminishes. Thus in the fundamental series the term may indeed be written in the Balmer form. In certain elements lines have been found which can be expressed by

and $4f - mx$, where $m = 5, 6$, etc.
$5x - my$, where $m = 6, 7$, etc.

The characteristic azimuthal quantum numbers will be 5 and 6 respectively, and the variable terms in both these series can be accurately expressed by

$$N/m^2,$$

where $m = 5, 6$, etc, and 6, 7, etc., respectively.

Thus far the allocation of the characteristic azimuthal quantum numbers has been based on what may be described as a justifiable assumption, but conviction as to the correctness of this follows at once from what is known as the principle of selection. In 1918 Rubinowicz [1] formulated a principle according to which changes or transitions in the azimuthal quantum number are limited to certain definite values, the radial quantum number being free to undergo any integral transition. The argument was based on the conservation of the moment of momentum and need not be entered into here. The principle of selection is associated with the rule of polarisation, and these may be stated as follows :—

1. *The Principle of Selection.*—The azimuthal quantum number can at most alter only by one unit at a time in changes of configuration of the atom. The maximum transition is, therefore, expressed by $k \rightarrow k \pm 1$.

2. *The Rule of Polarisation.*—If the azimuthal quantum number changes by ± 1, the emitted light is circularly polarised. If the azimuthal quantum number remains unchanged, only linear polarisation can occur.

In short, under the conditions we are at present concerned with every spectrum line must be due to a change in configuration of the atom involving the transition in the azimuthal quantum number $k \rightarrow k \pm 1$. The rule of polarisation does not come under consideration at the moment because the atoms are not in any way oriented, this only being the case when there is an external field. When such is the case the limits set by the principle of selection disappear and we find transitions in the azimuthal quantum number $\Delta k = 0$ or ± 2.

When the principle of selection is applied to the possible combinations between the various spectral terms, it becomes obvious that under ordinary conditions of excitation only those combinations may be expected which involve a change of one unit in the azimuthal quantum number. It may be seen at once that these permitted

[1] *Phys. Zeitsch.*, **19**, 441, 465 (1918).

combinations are the very ones which give rise to the four chief series shown by atoms not of the hydrogen type, thus :—

Type of Series.		Transition in k.
Principal series,	$1s - mp$	$2 \rightarrow 1$
Sharp series,	$2p - ms$	$1 \rightarrow 2$
Diffuse series,	$2p - md$	$3 \rightarrow 2$
Fundamental series,	$3d - mf$	$4 \rightarrow 3$

The reason why these four series have come to be looked on as the four chief series is to be found in the fact that the lines given by the above transitions are the most intense, because the initial quantum number m ($r = 0$) is the smallest possible within each type of combination. The principle of selection also permits the combinations

$$2s - mp \quad \text{and} \quad 3s - mp,$$

and such have been actually observed. The intensity of the lines given by these combinations is smaller than those of the true principal series, because m must then be greater than 2 in order to render possible an emission of energy. The same argument applies to the combinations $3p - md$, $4p - md$, $3d - mp$, and $4f - md$. As regards the series $4f - mx$ with the azimuthal quantum number transition $5 \rightarrow 4$, the lines generally lie in the infra-red region, but in the case of enhanced spectra they are shifted into the visible region. Fowler [1] found such a series in the spectrum of Mg^+ and he attributed them to the combination $4f - mf$, noting that calculated and observed values did not agree very closely. As a matter of fact the combination $4f - mf$ is forbidden by the principle of selection, since it involves the transition $k \rightarrow k$ in the azimuthal quantum number. It was Rojdestvensky [2] who offered the true explanation, namely, that the lines arise from the combination $4f - mx$.

It may be stated that those combinations which are permitted in the first instance by the principle of selection lead to the four most commonly occurring and most intense series. Other combinations are also permitted, but these occur more rarely and the resulting lines are less intense.

Reference has already been made to the fact that in the presence of an external field the principle of selection no longer holds. For instance, in the presence of a strong electric field lines have been observed which are invisible in the absence of such field. For example, the combinations $2p - mp(k \rightarrow k)$, $2s - md$ $(k \rightarrow k - 2)$ are cases in point. Since it is quite possible by the use of a very powerful discharge to produce an incipient electric field, some confusion has arisen as to the correctness of the rigid restriction set by the principle of selection, but it must be understood that the foregoing only applies to the condition of complete absence of an external field.

[1] *Phil. Trans.*, **214**, A, 225 (1914).
[2] *Verh. des. opt. Inst. in Petersburg*, No. **8**, Berlin, 1921.

Now the Ritz combination principle, as ordinarily stated, leads to the view that any combination is possible between any two spectral terms whatever. We now see that the selection principle sets a limitation to this too broad generalisation, and Sommerfeld substitutes a more precise statement, namely, that every series term can naturally be combined with any other series term of which the azimuthal quantum number differs by one unit from that of the first. Combinations which do not obey this limitation are not necessarily forbidden, but they require special conditions for their excitation.

The Multiplicity of Series Terms and the Inner Quantum Number.—In the last section the various series were treated as if they were all simple, whereas it is well known that they are complex. This is due to the fact that the principal, diffuse, and fundamental terms are not simple, but are two-fold or three-fold as the case may be. As was explained previously (p. 31) this is expressed by the formulæ

Principal series,	$1s - mp_i$	where $i = 1$ and 2, or 1, 2, 3.
Sharp series,	$2p_i - ms$	
Diffuse series,	$2p_i - md_i$	
Fundamental series,	$3d_i - mf_i$	

It is a well-established fact that the principal series consists of doublets or triplets with decreasing separation as m increases, whereas the sharp series consists of doublets or triplets with constant separation. We have also the well-established fact that the doublets or triplets in the diffuse and fundamental series are always composite, that is to say, satellites are always present in addition to the chief lines. It is an obvious deduction from this that the sharp term is always a simple term, the multiplicity being confined to the principal, diffuse, and fundamental terms. This deduction forms our starting-point in all that follows.

The first point to be noticed is that the p-, d-, and f-terms have always the same multiplicity, that is to say, they are all two-fold or three-fold so far as we have found as yet. This phenomenon is called by Sommerfeld the permanence of multiplicities and the question arises as to its explanation.

In dealing with these multiple terms the convention has been adopted of numbering the terms within each series in order of their magnitude, thus

$$mp_1 < mp_2 < mp_3\,;\ md_1 < md_2 < md_3\,;\ mf_1 < mf_2 < mf_3,$$

where of course the third terms are non-existent in doublet systems.

The second point to be noted is that the observed structure of the composite doublets or triplets in the diffuse and fundamental series is not as complex as would be expected on the combination principle. For example, in a diffuse doublet,

$$2\pi_i - m\delta_i, \quad \text{where } i = 1 \text{ and } 2,$$

it would be expected that there should be four lines—

$$2\pi_1 - m\delta_1,$$
$$2\pi_2 - m\delta_1,$$
$$2\pi_1 - m\delta_2,$$
$$2\pi_2 - m\delta_2,$$

but only three are observed. Similarly in a diffuse triplet we would expect nine lines, but only six are observed. This observed structure is true of all diffuse doublets and triplets, and consequently we are forced to the conclusion that out of the total number of combinations which are algebraically possible a definite number are physically impossible and forbidden by some principle of selection.

These phenomena are obviously incapable of explanation by the azimuthal quantum number alone, which is 2, 3, and 4 for all the multiple principal, diffuse, and fundamental terms, respectively.

The Inner Quantum Number.—Although the existence of the additional electric field gives a thoroughly satisfactory explanation of the resolution of the single Balmer series shown by atoms of the hydrogen type into series systems as exhibited by atoms not of the hydrogen type, this field does not account for the term multiplicities, that is to say, it does not explain the fact that the series systems are doublets or triplets. In order to explain this phenomenon Sommerfeld invokes an intra-atomic magnetic field. That such magnetic fields do exist is clearly established by the phenomena of the anomalous Zeeman effect as experimentally demonstrated by Paschen and Back.[1] It would seem too that the intra-atomic field causing the term multiplicities is produced by the orbits of the outer electrons of atoms. We know that atoms having the same valency in the chemical sense exhibit multiplicities of the same type, and that the multiplicities are even in the arc spectra of atoms of uneven valency, and uneven with atoms of even valency. Since the valency is determined by the number of outer electrons of the atom, the origin of the inner magnetic field would seem to be founded on the number and motion of these outer electrons.

Sommerfeld [2] attacks the problem from the point of view of the multiplicities of the diffuse series, where, as has already been shown, certain combinations which are algebraically possible are physically impossible, that is to say they are forbidden. This indicates that the azimuthal quantum number k is not sufficient for all purposes. This quantum number is 2 for all principal terms, 3 for all diffuse terms, and so on, and therefore it obviously cannot effect a determinate selection between the terms p_i or d_i. It follows that if the missing lines of the (pd) combination are forbidden by a principle of selection, it is necessary to introduce a new quantum number, which may be called the inner quantum number and designated by i.

[1] *Physica*, Zeeman Jubilee Number (1921), p. 261.
[2] *Ann. der Phys.*, **63**, 221 (1920).

In order to understand the procedure reference may be made to Fig. 4, where for a doublet system the series of terms is drawn on a scale of energy levels, the vertical arrows representing the transitions which gives rise to spectrum lines.

In the diagram the sharp term is lowest, having the greatest negative energy. This term has the azimuthal quantum number $k = 1$ and since the sharp terms are always single, we give it the inner quantum number $i = 1$. The π-levels lie next in order above this term and beginning from the top these are numbered π_1 and π_2, since $\pi_1 < \pi_2$. The azimuthal quantum number of both π-levels is $k = 2$ and the inner quantum numbers $i = 1$ and $i = 2$ are assigned to the π_2- and π_1-levels respectively. The δ-levels come next and these have as azimuthal quantum number $k = 3$, and to δ_2 and δ_1 are assigned the inner quantum numbers $i = 2$ and $i = 3$. To the fundamental levels ϕ_2 and ϕ_1, with azimuthal quantum number $k = 4$, are assigned the inner quantum numbers $i = 3$ and $i = 4$ respectively. In general, $i = k$ for the upper levels of the two-fold terms and $i = k - 1$ for the lower levels, whilst $i = 1$ always for the sharp terms.

Sommerfeld formulates two rules for the inner quantum numbers, namely, a principle of selection and a rule of intensity. We have already seen that except under special conditions the azimuthal quantum number can only undergo the transitions

$$k \rightarrow k \pm 1,$$

and his selection principle for the inner quantum numbers states that these only undergo the transitions

$$i \rightarrow i \pm 1 \quad \text{and} \quad i \rightarrow i \qquad . \qquad . \qquad . \qquad (13)$$

The rule of intensity states that of the three transitions permitted by (13) that one is to occur with greatest intensity which takes place in the same direction as the transition in the azimuthal quantum number; the intensity is to decrease the more the type of transition of i differs from that of k. It is possible, therefore, to speak of a strong, less strong, and weak transition, and these indications of intensity will be used in what follows.

We may now apply the principle of selection and the rule of intensity to the possible combinations between the levels shown in Fig. 4. In the first place, we may consider the first doublet of the principal series

$$\nu_1 = 1\sigma - \pi_1$$
$$\nu_2 = 1\sigma - \pi_2,$$

in which the azimuthal quantum number undergoes the transition $2 \rightarrow 1$. In the first of these the inner quantum number undergoes the transition $2 \rightarrow 1$ and, since this is in the same direction as the transition in the azimuthal quantum number, the intensity will be strong. In the second, the inner quantum number undergoes the transition $1 \rightarrow 1$ and consequently the resulting line will be less strong. Since $\pi_1 < \pi_2$, ν_2 is greater than ν_1 and thus the more refrangible line

of the pair will be the more intense as, for example, is shown in the D lines of sodium, where D_2 has twice the intensity of D_1. This difference of intensity in the principal pairs of the alkalies is still more pronounced in the higher members of the series.

The application of the principle of selection may be seen in the pairs of the diffuse series and the fundamental series. In the former

$$\nu = \pi_i - \delta_i,$$

involving the transition $3 \rightarrow 2$ in the azimuthal quantum number. We first of all have the two strong lines given by $\pi_1 - \delta_1$, and $\pi_2 - \delta_2$, where the inner quantum numbers undergo the transitions $3 \rightarrow 2$ and $2 \rightarrow 1$ respectively, that is in the same direction as the transition in the azimuthal quantum number. We next have the line given by $\pi_1 - \delta_2$ which is less strong because the transition $2 \rightarrow 2$ in the inner

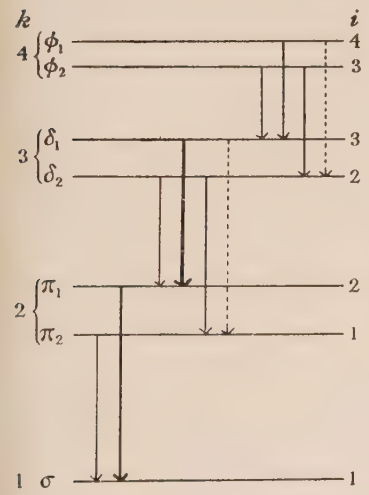

Fig. 4.

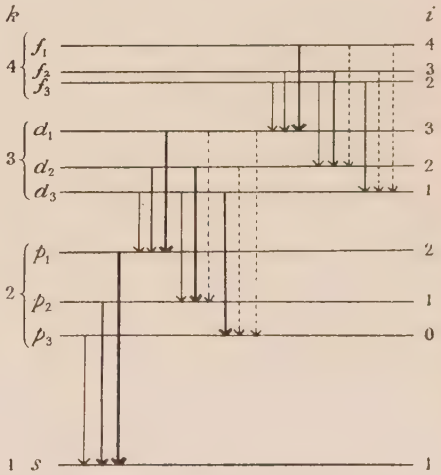

Fig. 5.

quantum number is not in the same direction as that in the azimuthal quantum number. The transition $\pi_2 - \delta_1$ is forbidden, since it involves the transition $3 \rightarrow 1$ in the inner quantum number, that is a change of two units. This line therefore is absent, as we have already learned.

Exactly similar conditions occur in the fundamental series where the transition $\delta_2 - \phi_1$ is forbidden, since it involves the transition of $4 \rightarrow 2$ in the inner quantum number, whilst the other three possible transitions take place with the production of lines having the relative intensities as observed.

In the triplet systems the scheme of inner quantum numbers must be extended and this is shown in the scheme of levels depicted in Fig. 5.

Here again in the highest level in each term the inner quantum number i has the same value as the azimuthal quantum number for that term, and decreases by unity at each step downwards within that term. The inner quantum number, therefore, decreases by two steps of unity from 4 to 2 in the fundamental levels, from 3 to 1 in the diffuse levels, and from 2 to 0 in the principal levels.

In considering the various transitions we may, as before, take first those between the p- and s-levels. Here there are no transitions forbidden by the principle of selection in the inner quantum numbers, but the resulting lines have three different intensities. The strongest intensity will be given by the combination $1s - p_1$, since the transition in the inner quantum number is in the same direction as that in the azimuthal quantum number. A less strong line will be given by the combination $1s - p_2$ involving the transition in the inner quantum number $1 \rightarrow 1$, whilst a weak line will be given by $1s - p_3$ since the transition in the inner quantum number $0 \rightarrow 1$ is in the opposite direction to that in the azimuthal quantum number. As we have $p_1 < p_2 < p_3$ it follows that in the principal series the triplet will decrease in intensity towards the longer wave-lengths, the opposite being the case for the sharp triplets.

In the diffuse series involving the combination $p_i - d_i$, the azimuthal quantum number transition is $3 \rightarrow 2$, and consequently we have three strong lines given by the inner quantum number transitions $3 \rightarrow 2$, $2 \rightarrow 1$, and $1 \rightarrow 0$, that is to say, the combinations $p_1 - d_1$, $p_2 - d_2$, and $p_3 - d_3$. Similarly, the combinations $p_1 - d_2$ and $p_2 - d_3$ give less strong lines since in these the inner quantum number undergoes the transitions $2 \rightarrow 2$ and $1 \rightarrow 1$. The combination $p_1 - d_3$ gives a weak line since the inner quantum number transition $1 \rightarrow 2$ is in the opposite direction to the transition in the azimuthal quantum number. The three combinations $p_2 - d_1$, $p_3 - d_2$, $p_3 - d_1$ are forbidden by our selection principle, since they involve transitions in the inner quantum number which are greater than unity, namely $3 \rightarrow 1$, $2 \rightarrow 0$, and $3 \rightarrow 0$, respectively.

As may be seen from Fig. 5, exactly similar results are obtained in the fundamental series $d_i - f_i$. We therefore see that in a diffuse series of doublets only three lines are possible out of four algebraic combinations, and that in a diffuse series of triplets only six are possible out of nine algebraic combinations. This agrees entirely with the observed facts.

Sommerfeld also considers some of the more complex combinations in the light of the conception of the inner quantum number, and two of these may be mentioned. In the first place, we have the combinations between the triplet and simple terms which occur with the divalent elements and these are represented schematically by the energy level diagram shown in Fig. 6.

By observation we know that the following combinations are permissible, (Sp_2), (Pd_2), (Pd_3), (p_1D), (p_2D), whilst the following combinations do not occur and therefore must be forbidden, (Sp_1), (Sp_3),

(Pd_1), (p_3D), and the question arises as to the values of the quantum numbers of the simple terms which exclude the latter four combinations. There can of course be no doubt about the azimuthal quantum numbers, which must be 1, 2, and 3, for S, P, and D respectively. The fact that certain combinations are forbidden indicates that the inner quantum numbers of these terms must be effective. Landé [1] assigned the values $i = 0, 1, 2$ for S, P, D, and this at once explains why the combinations (Sp_1), (Pd_1), and (p_3D) are forbidden, since they involve the transitions in the inner quantum number $2 \rightarrow 0$, $3 \rightarrow 1$, and $2 \rightarrow 0$ respectively.

A difficulty arises in connection with the exclusion of Sp_3, which involves the transition $0 \rightarrow 0$. In order to explain this Landé stated that this transition does not give a less strong line as our rule of intensity leads us to expect, but that it must not occur at all. The intensities of the permitted transitions are indicated by the thickness

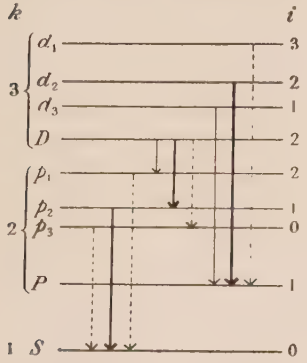

FIG. 6.

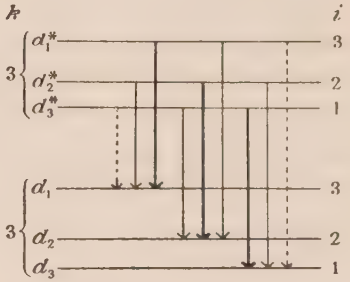

FIG. 7.

of the arrows, and these agree entirely with those that have been observed.

A second most interesting case is that afforded by the complex triplet system first noted by Rydberg in the spectra of calcium and strontium. These are due to the combinations ($p_i p_i^*$) and ($d_i d_i^*$), where p_i and d_i are the normal principal and diffuse terms which together give the composite diffuse triplets. Since the azimuthal number of d_i and d_i^* is 3, and that of p_i and p_i^* is 2, the combinations ($d_i d_i^*$) and ($p_i p_i^*$) contravene the selection principle affecting the azimuthal quantum number, this principle as stated above restricting the transitions to $k \rightarrow k \pm 1$.[2]

The diagrammatic scheme of levels of the ($d_i d_i^*$) group is shown in Fig. 7, the d_i^*-levels being drawn above the d_i-levels, since they

[1] *Phys. Zeitsch.*, **22**, 417 (1921).

[2] The occurrence and explanation of these so-called "asterisk" terms will be discussed later (see pp. 202 and 290). The transitions involving $\Delta k = 0$ are only possible when there is a simultaneous change in the atomic trunk.

are the initial levels. The permitted and forbidden transitions are shown as usual by the full and dotted arrows, the azimuthal quantum numbers being shown on the left, and the inner quantum numbers on the right. Two transitions are possible to d_1, namely $d_1 - d_1^*$ and $d_1 - d_2^*$, whilst the transition $d_1 - d_3^*$ is forbidden, since it involves an increase of two units in the inner quantum number. None of the three possible transitions with d_2 as the final level are forbidden, and the same is true of the two transitions $d_3 - d_2^*$ and $d_3 - d_3^*$. On the other hand, the transition $d_3 - d_1^*$ is excluded because it involves a decrease of two units in the inner quantum number.

The relative intensities of the spectrum lines given by the permitted transitions are of considerable interest. The transition in the azimuthal quantum number is $\Delta k = 0$ and consequently those transitions in the inner atomic number for which $\Delta i = 0$ must be regarded as taking place in the same direction as the transition in the former. It follows that in the present case the strongest lines will be given by the three inner quantum number transitions $3 \to 3$, $2 \to 2$, and $1 \to 1$, that is to say, the combinations $d_1 - d_1^*$, $d_2 - d_2^*$, $d_3 - d_3^*$. Less strong lines will be given by the combinations $d_1 - d_2^*$, $d_2 - d_1^*$, $d_2 - d_3^*$, and $d_3 - d_2^*$, where the transitions in the inner quantum numbers are $2 \to 3$, $3 \to 2$, $1 \to 2$, and $2 \to 1$, respectively. It follows from this that the structure of the composite triplet will consist of three principal lines, the two outer components having each a single satellite, and the middle component having two satellites. The satellites to the two outer components will be situated on opposite sides of their " parent " lines, whilst the central component will have a satellite situated on each side of it. This structure is fundamentally different from that of the normal composite diffuse triplets exhibited by the alkaline earth metals.

The combinations $(p_i p_i^*)$ also shown by these metals are analogous to the $(d_i d_i^*)$ combinations just described, but owing to the difference in the inner quantum numbers there is one essential difference. In a triplet p-term the inner quantum numbers are 2, 1, 0 instead of 3, 2, 1 as in the case of the diffuse triplet term (see Fig. 5). We have, therefore, in the present case the combination $p_3 - p_3^*$, which involves the transition in the inner quantum number $0 \to 0$. It was noted previously on p. 117 in the case of combinations between single and triplet terms, that the transition $S - p_3$ does not occur and in order to explain the absence of this line Landé stated that the transition $0 \to 0$ in the inner quantum number must be excluded. Now the line due to the transition $p_3 - p_3^*$ in the present case does not occur, that is to say, once again the transition in the inner quantum number $0 \to 0$ is excluded. The special convention set up in the previous case is, therefore, found to hold good under quite different conditions. As the result of the exclusion of the line due to the combination $p_3 - p_3^*$, the complex triplet $(p_i p_i^*)$ consists of $2 + 3 + 1$ lines, whereas the complex triplet $(d_i d_i^*)$ consists of $2 + 3 + 2$ lines, the normal complex diffuse triplet consisting of $3 + 2 + 1$ lines.

The evidence here set forth leaves little doubt as to the reality of the inner quantum numbers, although, as far as we have been able as yet to develop them, there still remains an element of empiricism about them. It might be thought indeed that the whole idea of the inner quantum number is an *ad hoc* conception, remarkably successful though it undoubtedly is in offering an explanation of doublet and triplet systems of series.

As a matter of fact, however, this theory of Sommerfeld's is one of the most important of all the results which have accrued from the Bohr theory. Not only does it form an integral part of the theory of the Zeeman effect, which indeed owes its complete solution to Sommerfeld's conception of the inner quantum number, but, when it was found that series systems exist of far greater complexity than the simple doublets and triplets we have had under review, these at once found their explanation by the inner quantum number, and the Sommerfeld theory was placed on a firm physical basis, thereby losing the element of empiricism to which I have referred. This could not have been achieved had it not been for the discovery of the more complex series systems, and for this reason I view the work by Catalan on the structure of the spectra of manganese and chromium, which work opened out an entirely new field, as one of the most important of all contributions to our knowledge of spectral series on the experimental side. Catalan himself extended this work to other spectra, and several other experimenters followed his lead, with the result that in a very short period of time his initial advance was consolidated and the whole question of series systems found a satisfactory and, I think, a complete solution.

Catalan's Work on the Multiplets in the Spectra of Manganese and Chromium.—A great step forward in the elucidation of the more complex spectra was taken by Catalan [1] in Fowler's laboratory. He succeeded in establishing the existence of groups of lines in the spectra of manganese and chromium which are very much more complex than the groups exhibited by the alkaline earth metals. This work has more recently been extended by Catalan himself and others, and the importance of it lies in the fact that it has led to a much deeper understanding of the phenomena of series architecture and of atomic structure. It has in particular enabled Sommerfeld, and after him Landé, to place the somewhat empirical notion of the inner quantum numbers on a true physical basis, and it has also rendered in the hands of Back and of Landé signal service in solving the problem of the Zeeman effect.

In order that a clear perspective of this advance and of its great importance may be gained it is necessary to consider Catalan's investigations of the spectrum of manganese in some detail, particularly with the view of understanding how he arrived at the existence of the complex groups. As far back as 1894 Kayser and Runge recognised

[1] *Phil. Trans.*, **223**, A, 127 (1922).

in the arc spectrum of manganese five triplets which they assigned in part to a sharp series and in part to a diffuse series. Catalan succeeded in extending these series and in recognising the corresponding principal series of triplets. The wave-lengths and wave-numbers of the lines of what may be called, in view of what follows, the ordinary triplet series of manganese are given in Table XLV.

TABLE XLV.

The Ordinary Triplet Series of Manganese.

Principal, $1s - mp$.

$1s = 20506{\cdot}13$.

λ.	Int.			m.	$mp_{1,2,3}$
— 4823·522	10R	— 20725·96	173·71		41232·09
— 4783·432	9R	— 20899·67	129·18	1	41405·80
— 4754·048	9R	— 21028·85			41534·98
15263·1		6550·0		2	13956·1
7646·34	3*n*	13074·56	9·52		7431·57
7651·91	3d	13065·04	7·38	3	7441·09
7656·24	2*n*	13057·66			7448·47
6315·064	2	15830·78		4 ?	4675·35

Sharp, $1p - ms$.

$1p_1 = 41232{\cdot}09$ $1p_2 = 41405{\cdot}80$ $1p_3 = 41534{\cdot}98$

λ.	Int.			m.	ms.
4823·522	10R	20725·96	173·71		
4783·432	9R	20899·67	129·18	1	20506·13
4754·048	9R	21028·85			
3178·508	6	31452·24	173·63		
3161·055	5	31625·87	129·22	2	9779·89
3148·192	4	31755·09			
2818·09	3	35474·8	173·5		
2804·35	2	35648·3	129·2	3	5757·4
2794·23	2	35777·5			
2670·22	2	37439·0	173·8		
2657·88	1	37612·8	129·0	4	3793·1
2648·79	1	37741·8			
2595·77	4	38512·7	173·7		
2584·12	3	38686·4	129·2	5 (?)	2719·4
2575·51	5	38815·6			

Diffuse, $1p - md$.

λ.	Int.				*m.*
3570·034	7R	28002·97			
3569·798	9R	28004·82	1·85		
3569·499	10R	28007·16	2·34	$md_1 = 13224{\cdot}93$	
			173·71	md_2 13227·27	
3548·180	7·5R	28175·44			
3548·024	8R	28176·68	1·24		
3547·792	8·5R	28178·52	1·84	$md_3 = 13229{\cdot}12$	2
			129·17	$md_4 = 13230{\cdot}38$	
3532·110	8R	28303·68			
3531·990	7·8R	28304·58	0·90		
3531·833	7·5R	28305·85	1·27	$md_5 = 13231{\cdot}30$	
2940·51	7*n*	33997·8			
2925·59	6*n*	34171·2	173·4		
2914·62	6*n*	34299·8	128·6	7234·7	3
2726·15	4*n*	36670·9			
2713·35	3*n*	36844·0	173·1		
2703·98	3*n*	36972·6	128·6	4561·8	4
2624·80	2	38086·7			
2612·86	2	38260·8	174·1		
2604·21	1	38389·4	128·6	3145·3	5

Fundamental, $2d_1 - mf$.

λ.		*m.*	*mf.*
15964·9	6262·0	3	6962·9
11377·9	8786·6	4	4438·3

Combination lines.

λ.	Int.		Calc.
3664·624	1	27280·18	$1p_1 - 2p = 27276{\cdot}0$
3642·662	1	27444·65	$1p_2 - 2p = 27449{\cdot}7$
7383·59	1	13539·82	$1s - 3f = 13543{\cdot}2$

As can be seen three members of the sharp series of triplets ($1p - ms$) have been identified and the wave-number differences are 173·7 and 129·2 respectively. In the diffuse series $1p - md$ the complete triplet consists of nine lines, which, however, have only been identified in the case of the first member. Some difficulty was caused by the fact that the lines are grouped together in sets of three, and in each set the lines are very close together. Furthermore, the lines are very diffuse, with a strong tendency to reversal, so that their resolution is difficult. The best results were obtained by the use of carbon poles with a small quantity of a manganese salt, in order to guard against the reversal by the surrounding vapour. It will be noticed that the *d*-term is five-fold instead of three-fold as in the case of the alkaline earths. The structure of the first diffuse triplet may be represented as follows :—

				7·5R		8R		8R
				28305·85	1·27	28304·58	0·90	28303·68
				129·17		129·14		
		8·5R		8R		7·5R		
		28178·52	1·84	28176·68	1·24	28175·44		
		173·70		173·71				
10R		9R		7R				
28007·16	2·34	28004·82	1·85	28002·97				

The intensities are given above each component and the small numbers express the wave-number differences.

From the sharp and diffuse series the lines belonging to the principal and fundamental series of triplets, together with the three combination lines, have been identified, as shown in the table.

In the arc spectra of the metals of the alkaline earths there exist the singlet series and also certain inter-combination lines formed by combinations of the singlet with the triplet terms. Amongst the latter the lines $1S - 1p_2$ and $1S - 1p_3$ are of particular importance, the combination line $1S - 1p_1$ never being present. Further, the line $1S - 1p_2$ is always stronger than the line $1S - 1p_3$ and indeed the former in certain cases appears alone; it has important characteristics. In magnesium this line ($\lambda = 4571$) has long been recognised as being especially characteristic of the flame spectrum and it is strongly developed in the electric furnace spectrum at the lowest temperature. Furthermore this line $1S - 1p_2$ is the resonance line of magnesium, calcium, and other elements.

From these considerations it would follow that if these lines $1S - 1p_2$ and $1S - 1p_3$ occur in the spectrum of manganese, there should appear two lines with separation $\Delta\nu = 129{\cdot}2$ ($1p_3 - 1p_2 = 129{\cdot}18$) and strong at low temperatures. Calatan found that the two lines

5394·677 (7)	18531·65	$\Delta\nu = 129{\cdot}14.$
5432·555 (5)	18402·51	

satisfied the conditions, and his conclusions were entirely justified by King's statement [1] that these lines are remarkable for their strength at low temperatures in the electric furnace spectrum.

Accepting the allocation of these two lines, we now can evaluate the term 1S, since $1p_2$ and $1p_3$ are known (see Table XLV.), thus

$$1S - 1p_2 = 18531{\cdot}65, \qquad 1S = 18531{\cdot}65 + 41405{\cdot}80 = 59937{\cdot}45$$
$$1S - 1p_3 = 18402{\cdot}51, \qquad 1S = 18402{\cdot}51 + 41534{\cdot}98 = 59937{\cdot}49$$
$$\text{Mean } 1S = 59937{\cdot}47.$$

With this value of 1S at our command we may now investigate the singlet system of manganese, and naturally the first line to be looked for is the first member of the principal series of singlets $1S - 1P$.

[1] *Astrophys. Journ.*, **53**, 133 (1921); see also vol. ii., p. 62.

Now in other elements this line has very characteristic properties, being extremely persistent at low temperatures and very easily and strongly reversed. When an element is present as an impurity, the most probable line to appear is 1S — 1P. In many elements the term 1P has a value not very different from 24000 and consequently an approximate value of P(1) may be obtained from the difference

$$1S - 1P = 60000 - 24000 = 36000 \quad \text{or} \quad \lambda = 2780.$$

There is no single line in the manganese spectrum near this wave-length having the specified characteristics, but there is a strongly reversed triplet, namely,

λ.		ν.	
2794·822	(10R)	35769·94	$\Delta\nu = 44{\cdot}12$
2798·273	(9R)	35725·82	$\Delta\nu = 35{\cdot}75$
2801·076	(8R)	35690·07	

This group is found as an impurity in many other spectra and consequently Catalan was convinced that they represent the term 1S — 1P. Considered as the first member of the sharp series this triplet should be negative, that is to say, the weakest line will be on the red side and this is actually the case. There should exist therefore additional triplets of the sharp series with separations of 44·1 and 35·75.

Paulson [1] and Meggers and Kiess [2] noted the existence of the wave-number difference 35·8 in the spectrum of manganese and Catalan gives the following triplets :—

λ.		ν.	Δν.
7326·55	(7)	13645·25	
7302·92	(6)	13689·38	44·13
7283·80	(6)	13725·33	35·95
5457·468	(1)	18318·44	
5470·640	(8)	18274·33	44·11
5481·395	(6)	18238·48	35·85

The intensities of the lines of the second triplet are not in the usual order and, as will presently be shown, they form part of a more complex group which also includes two more lines at λ — 5505·877 and 5516·773 with separation of 35·86.

Another triplet was found with normal distribution of intensities as follows :—

λ.		ν.	Δν.
6605·546	(3)	15134·62	
6586·357	(2)	15178·79	44·17
6570·830	(2)	15214·59	35·80

[1] *Astrophys. Journ.*, **40**, 300 (1914).
[2] Bureau of Standards, *Sc. Papers*, No. 372 (1920).

Assuming that the first triplet at $\lambda = 2795$, 2798, and 2801 is $1S - 1P_i$, then from the value $1S = 59937{\cdot}47$, calculated above, we have

$$1P_1 = 59937{\cdot}47 - 35769{\cdot}94 = 24167{\cdot}53$$
$$1P_2 = 59937{\cdot}47 - 35725{\cdot}82 = 24211{\cdot}65$$
$$1P_3 = 59937{\cdot}47 - 35690{\cdot}07 = 24247{\cdot}40$$

It is obvious that all triplets having separations of 44·1 and 35·8 must be combinations of $1P_i$ with unknown terms x, y, z, etc. Calculating the values of these terms from the triplets given above, we have

$$\left.\begin{array}{ll} 15134{\cdot}62 = 1P_1 - x & x = 9032{\cdot}91 \\ 15178{\cdot}79 = 1P_2 - x & x = 9032{\cdot}86 \\ 15214{\cdot}59 = 1P_3 - x & x = 9032{\cdot}81 \end{array}\right\} \text{Mean} = 9032{\cdot}86.$$

$$\left.\begin{array}{ll} 13645{\cdot}25 = 1P_1 - y & y = 10522{\cdot}28 \\ 13689{\cdot}38 = 1P_2 - y & y = 10522{\cdot}27 \\ 13725{\cdot}33 = 1P_3 - y & y = 10522{\cdot}07 \end{array}\right\} \text{Mean} = 10522{\cdot}21.$$

Now the two terms $1S = 59937{\cdot}47$ and $x = 9032{\cdot}86$ may be, from Rydberg's tables, two non-consecutive terms of the same series with another term between them of approximate value 18500. If this is the case the second triplet member $1P_i - 2S$ would be situated at about

$$24200 - 18500 = 5700 \quad \text{or} \quad \lambda = 17540.$$

A strong line at $\lambda = 17607{\cdot}5$ was observed by Randall and Barker[1] and there is little doubt that this is a line of the second triplet of the sharp series. In all probability therefore the term $y = 10522{\cdot}21$ is a diffuse term, namely, 3D.

Catalan next deals with the two narrow manganese triplets which are as follows :—

λ.		ν.	$\Delta\nu$.
4030·760	(10)	24802·23	
			14·22
4033·074	(9)	24788·01	
			8·70
4034·489	(9)	24779·31	
6021·787	(10)	16601·78	
			14·21
6016·636	(9)	16615·99	
			8·72.
6013·484	(9)	16624·71	

The first of these is a negative triplet and is thus similar to the triplet $1S - 1P_i$. It also is very strong in the flame spectrum and is usually reversed in the arc spectrum. King[2] drew attention to the extreme persistence of these lines and to the fact that they occur very generally as impurity lines in arc spectra. They constitute a prominent low temperature group and it is evident that they show many analogies to the triplet $1S - 1P_i$.

[1] *Astrophys. Journ.*, **49**, 59 (1919). [2] *Loc. cit.*

The difference between the wave-numbers of the first line of the present triplet and the first line of $1S - 1P_i$ is

$$35769{\cdot}94 - 24802{\cdot}23 = 10967{\cdot}71.$$

This difference is very nearly the same as that between the line $1P - 2S$ ($\lambda = 17607{\cdot}5$) and the first line of the second triplet given above ($\lambda = 6021{\cdot}787$), namely,

$$16601{\cdot}78 - 5677{\cdot}9 = 10923{\cdot}9.$$

That this is not a mere coincidence is shown by the fact that when all the triplets with separations 44·1 and 35·8 are tested, the following results are obtained. The first line of the triplet $1P - 3S$ ($\lambda = 6605{\cdot}546$) gives

$$15134{\cdot}62 + 10967{\cdot}7 = 26102{\cdot}3, \quad \text{or} \quad \lambda = 3829{\cdot}99.$$

There is a line at $\lambda = 3829{\cdot}987$ which forms the first line of the following triplet:—

λ.		ν.	Δν.
3829·987	(2)	26102·37	
			14·20
3827·904	(1)	26116·57	
			8·71.
3826·698	(1)	26125·28	

Clearly these separations are the same as those of the triplet at $\lambda = 4031$, 4033, and 4035.

Again, the first line of the triplet $1P - 3D$ ($\lambda = 7326{\cdot}55$) gives

$$13645{\cdot}25 + 10967{\cdot}7 = 24613{\cdot}0, \quad \text{or} \quad \lambda = 4061{\cdot}74.$$

There is a line at $\lambda = 4061{\cdot}744$ which forms the first line of the following triplet:—

λ.		ν.	Δν.
4061·744	(3)	24613·03	
			14·23
4059·399	(2)	24627·26	
			8·73.
4057·959	(2)	24635·99	

In Table XLVI. are given the two parallel systems of triplets, the first lines of the two systems being separated by $C = 10967{\cdot}75$. Catalan draws attention to the fact that this number is remarkably close to 1/10th of the Rydberg constant $N = 109678{\cdot}3$.

TABLE XLVI.

THE TWO PARALLEL SYSTEMS OF NARROW TRIPLET SERIES.

Principal, $1S - mP$. $1S = 59937{\cdot}47$.

λ.	Int.			m.	$mP_{1,2,3}$.
2794·822	10	35769·94			24167·53
			44·12		
2798·273	9	35725·82		1	24211·65
			35·75		
2801·076	9	35690·07			24247·40

TABLE XLVI.—*Continued.*

Principal, $1S - (mP + C)$.

λ.	Int.			*m*.	Shift number C.
4030·760	10	24802·23	14·22		10967·71
4033·074	9	24788·01	8·70	1	
4034·489	9	24779·31			

Sharp, $1P - mS$.

$1P_1 = 24167{\cdot}53$ $1P_2 = 24211{\cdot}65$ $1P_3 = 24247{\cdot}40$

λ.	Int.			*m*.	*m*S.
− 2794·822	10	− 35769·94	44·12		
− 2798·273	9	− 35725·82	35·75	1	59937·47
− 2801·076	9	− 35690·07			
17607·5		(5644·0) (5678·1) (5714·0)	44·1 35·8	2	18533·50
6605·546	3	15134·62	44·11		
6586·357	2	15178·79	35·80	3	9032·89
6570·830	2	15214·59			

Sharp, $(1P + C) - mS$.

λ.	Int.			*m*.	Shift number C.
− 4030·760	10	− 24802·23	14·22		10967·71
− 4033·074	9	− 24788·01	8·70	1	
− 4034·489	9	− 24779·31			
6021·787	8	16601·78	14·21		10967·75
6016·636	8	16615·99	8·72	2	
6013·489	7	16624·71			
3829·987	2	26102·37	14·20		10967·75
3827·904	1	26116·57	8·71	3	
3826·628	1	26125·28			

Diffuse, $1P - mD$.

$1P_1 = 24167{\cdot}53$ $1P_2 = 14211{\cdot}65$ $1P_3 = 24247{\cdot}40$

λ.	Int.			*m*.	*m*D.
7326·55	7	13645·25	44·13		
7302·92	6	13689·38	35·95	3	10524·27
7283·80	6	13725·33			

Diffuse, $(1P + C) - mD$.

λ.	Int.			*m*.	Shift number C.
4061·744	3	24613·03	14·23		10967·78
4059·399	2	24627·26	8·73	3	
4057·959	2	24635·99			

The Multiplets of Manganese. Catalan next deals with the occurrence in the manganese arc spectrum of line systems which are even more complex than the diffuse triplets already described. As will be

shown these line systems form groups with a definite structure and he assigns to them the name of multiplet. The first instance of this type of regularity was found in the blue region where there are many lines, and the nine most intense of these present the appearance of a diffuse triplet but with the satellites in the wrong order. The group contains the lines given in Table XLVII.

TABLE XLVII.

λ.		ν.	Class (King).
4455·019	(6)	22440·32	III.
4455·320	(6)	22438·80	III.
4455·820	(5)	22436·29	III.
4457·041	(5)	22430·14	III.
4457·553	(6)	22427·56	—
4458·263	(6)	22423·99	II.
4460·376	(3)	22413·37	—
4461·089	(6)	22409·84	III.
4462·033	(8R)	22405·85	III.

The multiplet has the following structure :—

				22436·29	2·51	22438·80	1·42	22440·32
				8·73		8·66		
		22423·99	3·57	22427·56	2·58	22430·14		
		14·15		14·19				
22405·05	4·80	22409·84	3·53	22413·37				

The separations 14·19 and 8·73 are the same as those of the series of narrow triplets previously described. The first line (λ = 4462·033) was tested with the constant C = 10967·75, thus

$$22405{\cdot}05 - 10967{\cdot}75 = 11437{\cdot}30, \quad \text{or} \quad \lambda = 8740{\cdot}92.$$

There is a line at λ = 8740·91 which forms the first line of the multiplet of nine lines which is given in Table XLVIII.

TABLE XLVIII.

λ.		ν.
8670·85	(2)	11529·71
8672·08	(2)	11528·09
8674·01	(2)	11525·53
8699·13	(2)	11492·24
8701·04	(2)	11489·72
8703·73	(3)	11486·17
8734·64	(1)	11445·53
8737·29	(2)	11442·05
8740·91	(3)	11437·32

The structure of this multiplet is as follows :—

				11525·53	2·56	11528·09	1·62	11529·71
				35·81		35·85		
		11486·17	3·55	11489·72	2·52	11492·24		
		44·12		44·19				
11437·32	4·73	11442·05	3·48	11445·53				

Here we find the separations of 44·1 and 35·8 previously noted in the case of the first system of narrow triplets given in Table XLVI. The separation of the first lines of these two multiplets is identical with that between the two systems of narrow triplets. The smaller separations are doubtless the same in the two multiplets—

		Separations.		
Blue multiplet . . .	4·80	3·57 3·53	2·51 2·58	1·42
Extreme red multiplet . .	4·73	3·55 3·48	2·56 2·52	1·62

Mention was made above of the pair of lines at $\lambda = 5505{\cdot}877$ and 5516·773 with separation 35·8, and of the negative triplet at $\lambda =$ 5457·468, 5470·640, and 5481·395 with separations of 35·8 and 44·1. Catalan shows that these lines belong to the multiplet of nine lines, shown in Table XLIX.

TABLE XLIX.

λ.		ν.	Class (King).
5341·070	(10)	18717·64	III.A
5407·432	(6)	18487·97	III.A
5420·368	(6)	18443·82	III.A
5457·468	(3)	18318·44	II.A
5470·640	(8)	18274·33	II.A
5481·395	(6)	18238·48	II.A
5505·877	(4)	18157·38	III.A
5516·773	(7)	18121·52	III.A
5537·749	(8)	18052·88	III.

which has the following structure :—

				18238·48 35·85	116·96	18121·52 35·86	68·64	18052·88
		18443·82 44·15	169·49	18274·33 44·11	116·95	18157·38		
18717·64	229·69	18487·97	169·53	18318·4				

The first line of this multiplet is tested with the constant difference C = 10967·75 and, remembering that the original triplet component was negative, we have

$$-18717{\cdot}64 + 10967{\cdot}75 = 7749{\cdot}89, \quad \text{or} \quad \lambda = 12899{\cdot}9.$$

Two lines at $\lambda = 12899{\cdot}7$ and 13294·1 were observed by Randall and Barker [1] and the separation is 229·9. This pair forms the basis of another nonet, of which however only six lines as yet have been observed. These are given in Table L., Randall and Barker's values being reduced to the international standard.

[1] *Loc. cit.*

TABLE L.

λ.		ν.
12899·7	(80)	7750·0
13294·1	(50)	7520·1
13317·9	(30)	7506·7
13625·7	(200)	7337·1
13863·8	(100)	7211·1
13997·0	(120)	7142·5

The complete scheme of the multiplet is as follows :—

				(7328·3) 8·8	117·2	7211·1 8·8	68·6	7142·5
		7506·7 13·4	169·6	7337·1 14·1	117·2	(7219·9)		
7750·5	229·9	7520·1	168·9	(7351·2)				

Now the two lines at $\lambda = 4018{\cdot}108$ and 4055·553 have separation of 229·7, and in this region there are altogether nine lines which can be grouped together with the four separations 229·7, 169·5, 116·9, and 68·6. The complete multiplet is, however, more complex than those already described and consists of thirteen lines which are all of the low temperature type. They are given in Table LI.

TABLE LI.

λ.		ν.	Class (King).
4018·108	(8)	24880·32	I.
4035·730	(5)	24771·69	I.
4041·366	(10R)	24737·15	I.
4048·760	(4)	24691·97	I.
4055·553	(8)	24650·62	I.
4058·936	(2)	24630·02	I.
4063·533	(4)	24602·18	I.
4068·029	(2)	24575·01	—
4070·280	(2)	24561·43	II.
4079·245	(6)	24507·44	I.
4079·428	(6)	24506·34	I.
4082·947	(6)	24485·22	I.
4083·639	(6)	24481·07	I.

The structure of this multiplet is as follows :—

						24630·06 55·05	68·63	24561·43 55·09
				24691·97 89·79	116·96	24575·01 89·79	68·67	24506·34
		24771·69 121·07	169·51	24602·18 121·13	116·96	24485·22		
24880·32 143·17	229·70	24650·62 143·18	169·57	24481·05				
24737·15	229·71	24507·44						

In addition to these multiplets which include all the recognised constant wave-number differences in the manganese arc spectrum, Catalan discovered other multiplets and these may now be detailed,

together with their structures. In the first place, we have one of nine lines given in Table LII.

TABLE LII.

λ.		ν.	Class (King).
3044·573	(6)	32835·76	III.
3054·836	(5)	32730·31	III.
3062·132	(4)	32647·52	III.
3066·035	(3)	32605·97	III.
3070·290	(5)	32560·77	III.
3073·144	(4)	32530·54	III.
3079·638	(5)	32461·95	IV.
3081·347	(4)	32443·94	IV.
3082·062 [1]	(2)	32436·42	—

with the following structure :—

				32647·52	116·98	32530·54	68·59	32461·95
				86·75		86·60		
		32730·31	169·54	32560·77	116·83	32443·94		
		124·34		124·35				
32835·76	229·79	32605·97	169·55	32436·42				

We next have a multiplet of fifteen lines given in Table LIII.

TABLE LIII.

λ.		ν.	Class (King).
3776·537	(1)	26471·79	—
3790·215	(3)	26376·19	III.
3799·256	(2)	26313·49	III.
3806·866	(10R)	26260·93	I.
3809·599	(6)	26242·07	II.
3816·746	(2)	26192·93	III.
3823·515	(9R)	26146·56	II.
3823·896	(5)	26143·94	II.
3829·674	(2)	26104·50	III.
3833·864	(6)	26075·92	II.
3834·363	(8R)	26072·58	II.
3838·329	(2)	26045·64	—
3839·777	(4)	26035·82	II.
3841·081	(5)	26026·97	II.
3843·985	(4)	26007·31	II.

having the following structure :—

								26045·64
								9·82
						26104·50	68·68	26035·82
						28·58		28·51
				26192·92	117·00	26075·92	68·61	26007·31
				48·98		48·95		
		26313·49	169·65	26143·94	116·97	26026·97		
		71·42		71·36				
26471·79	229·72	26242·07	169·49	26072·58				
95·52		95·51						
26376·27	229·71	26146·56						
115·34								
26260·93								

Lastly, there remains the multiplet of thirteen lines given in Table LIV.

[1] This line was first measured by Catalan.

TABLE LIV.

λ.		ν.	Class (King).
3206·915	(3)	31173·64	IV.
3212·897	(6)	31115·60	III.
3226·043	(2)	30998·81	IV.
3230·725	(3)	30943·90	III.
3236·787	(6)	30885·94	II.
3240·624	(3)	30849·38	IV.
3243·784	(4)	30819·32	III.
3248·521	(4)	30774·38	III.
3251·139	(3)	30749·60	IV.
3252·954	(4)	30732·45	III.
3256·141	(4)	30702·36	III.
3258·417	(4)	30680·92	III.
3260·237	(4)	30663·80	III.

with the following structure :—

						30749·60	68·68	30680·92
						17·15		17·12
				30849·38	116·93	30732·45	68·65	30663·80
				30·06		30·09		
		30988·81	169·49	30819·32	116·96	30702·36		
		44·91		44·94				
31173·64	229·74	30943·90	169·52	30774·38				
58·04		57·96						
31115·60	229·66	30885·94						

The nine multiplets and their characteristic separations are assembled in Table LV.

TABLE LV.

Limiting λ.	No. of lines.	Triplet separations.	Separations.		Non-recurring separations.	Remarks.
		14·2, 44·1	4·8, 3·5, 229·7, 169·5			
		8·7, 35·8	2·5, 1·4, 116·9, 68·6			
4462 — 4455	9	×	×			Interval = 10967·7
8741 — 8671	9	×	×			
5538 — 5341	9	×		×		Interval = 10967·7
13997 — 12900	9	×		×		
3630 — 3578	9			×	102, 103	
4084 — 4018	13			×	143, 121, 89, 53	
3082 — 3045	9			×	124, 86	
3844 — 3777	15			×	115, 95, 71, 48, 28, 10	
3260 — 3207	13			×	58, 44, 30, 17	

Catalan observed certain other groups of lines in which the same separations occurred more than once. The only one that need be mentioned here is a group of ten lines which shows the four separations of 229·7, 169·5, 116·9, and 68·6, and these are given in Table LVI.

TABLE LVI.

λ.		ν.	Class (King).
3240·408	(3)	30851·44	III.
3254·040	(2)	30722·19	IV.
3264·713	(4)	30621·76	III.
3278·553	(3)	30492·49	IV.
3296·029	(2)	30330·83	IV.
3296·884	(3)	30322·97	IV.
3308·791	(3)	30213·83	—
3316·324	(3)	30145·32	IV.
3343·728	(2)	29898·18	IV.
3351·427	(1)	29829·50	—

This group overlaps the last multiplet described above, but no relation between the two has been found. The relation between the lines of the present group may be shown as follows :—

30851·44 229·68 30621·76
30722·19 229·70 30492·49 169·52 30832·97
30330·83 117·06 30213·83 68·51 30145·32
29898·18 68·68 29829·50

Catalan next deals with the enhanced spectrum of manganese, and it is interesting to note that he was able to detect triplets and a multiplet which are strikingly similar to those found in the spectrum of the neutral manganese atom. In the first place, there are present in the spectrum of Mn^+ three very prominent lines, which exhibit themselves as fairly strong lines in the arc spectrum, but are considerably strengthened on passing from the arc to the spark. The behaviour of these lines, moreover, in the electric furnace spectrum is very different from that of the diffuse arc triplet $1p - 3d$. The enhanced triplet is as follows :—

λ.		ν.	Δν.	Class (King).
2949·207	(10)	33897·54		IV.
			114·08	
2939·315	(9)	34011·62		V.
			72·45	
2933·066	(8)	34084·07		V.

There are two other strong triplets in the ultra-violet, one of which consists of three lines which are fairly strong in the arc spectrum and strongly reversed in the spark spectrum. This is a negative triplet as shown by the following measurements :—

λ.		ν.	Δν.
2576·116	(10R)	33806·52	
			263·58
2593·734	(9R)	33542·94	
			176·91.
2605·695	(9)	33366·03	

The other triplet is of the diffuse type and consists of nine lines as in the case of the diffuse triplet of neutral manganese. The component lines are given in Table LVII.

TABLE LVII.

λ.		ν.
2427·43	(3)	41183·3
2427·77	(4)	41177·5
2427·97	(4) ?	41174·1
2437·45	(5)	41015·7
2437·92	(3)	41006·1
2438·22	(3)	41001·1
2452·53	(10)	40761·9
2453·17	(2)	40751·3
2453·65	(1)	40743·0

and the triplet has the following structure :—

				41183·3	5·8	41177·5	3·4	41174·1
				177·2		176·4		
		41015·7	9·6	41006·1	5·0	41001·1		
		264·4		263·1				
40761·9	10·6	40751·3	8·3	40743·0				

The wider separations of this triplet are practically identical with those of the preceding negative triplet.

The enhanced lines given in Table LVIII. constitute a multiplet which is very similar to the arc multiplets.

TABLE LVIII.

λ.		ν.	Class (King).
3497·540	(6)	28583·37	V.
3496·815	(4)	28589·30	V.
3495·840	(8)	28597·26	V.
3488·618	(8)	28655·89	V.
3482·918	(7)	28703·37	V.
3474·139	(6)	28775·90	V.
3474·050	(7)	28776·65	V.
3460·332	(8)	28890·71	V.
3441·999	(9)	29045·93	V.

The structure of this multiplet is as follows :—

				28775·90	120·01	28655·89	58·63	28597·26
				72·53		72·52		
		28890·71	187·34	28703·37	120·00	28583·37		
		114·06		114·07				
29045·93	269·28	28776·65	187·35	28589·30				

The structure and intensity distribution are similar to those in the case of the nine line multiplets in the arc spectrum. Moreover, the separations 114·06 and 72·53 are identical with those of the enhanced triplet at $\lambda = 2949$, 2939, and 2933.

Catalan considers that the negative triplet ($\lambda = 2576$, 2594, and 2606) is the first member of the principal series $1s^+ - mp^+$ and the complex triplet to be a member of the diffuse series $1p^+ - md^+$. Since the strong enhanced triplet ($\lambda = 2949$, 2939, and 2933) is comparable in intensity with the narrow arc triplets of the S or D series, it is probably a member of the enhanced series S or D. The enhanced multiplet shown above, which shows the separations of the last-mentioned triplet, seems to be analogous to the arc multiplet at $\lambda = 5341$, which contains the separations of the arc S and D series. The evidence therefore led Catalan to the view that the enhanced lines form a complex triplet system which is built up on the same plan as the arc spectrum.

Although Catalan in his first paper did not complete his investigations into the arc spectrum of chromium, he was able to identify three multiplets which are given in Table LIX.

TABLE LIX.

Cr multiplet I.				Cr multiplet II.				Cr multiplet III.			
λ.	Int.	ν.	Class.	λ.	Int.	ν.	Class.	λ.	Int.	ν.	Class.
5247·55	6	19051·2	I.	3883·33	10	25743·8	I.	4337·58	20	23047·9	I.
5264·18	6	18991·0	I.	3885·21	8	25731·4	I.	4339·46	20	23037·9	I.
5265·73	6	18985·5	I.	3886·77	8	25721·0	I.	4339·74	12	23036·4	I.
5296·69	5	18874·4	I.	3894·05	7	25673·0	I.	4344·52	25	23011·1	I.
5298·29	7	18868·7	I.	3902·90	6	25614·8	II. ?	4351·05	15	22976·5	I.
5300·71	4	18860·2	I.	3903·14	5	25613·3	II.	4351·85	40	22972·5	I.
5345·80	7	18701·1	I.	3908·76	10	25576·4	II.	4359·65	20	22931·2	I.
5348·31	6	18692·3	I.	3916·26	6	25527·3	I.	4371·31	20	22870·1	I.
5409·81	8	18479·8	I.	3919·17	12R	25508·4	II.	4373·25	6	22859·9	I.
				3921·06	9	25496·1	I.	4384·98	20	22798·7	I.
				3928·67	10	25446·7	I.	4391·76	6	22763·4	I.
				3941·52	10	25363·8	I.	4412·27	6	22657·7	I.A.

The structure of the first multiplet is

				18874·4	116·6	18991·0	60·2	19051·2
				5·7		5·5		
		18701·1	167·6	18868·7	116·8	18985·5		
		8·8		8·5				
18479·8	212·5	18692·3	167·9	18860·2				

This multiplet contains the separations 8·5 and 5·7 of the series S and D, and also four separations which are remarkably close to the four important separations in the manganese spectra, thus :—

Cr . . .	212·5	167·8	116·7	60·2
Mn . . .	229·7	169·5	116·9	68·6
Mn^+ . . .	269·3	187·3	120·0	58·6

These four separations also occur in the second multiplet of chromium, which has the structure

				25496·1	117·2	25613·3	59·7	25673·0
				118·7		118·1		
		25446·7	168·1	25614·8	116·6	25731·4		
		129·7		129·0				
25363·8	212·6	25576·4	167·4	25743·8				
144·6		144·6						
25508·4	212·6	25721·0						

Many other lines are mixed with this multiplet, but only one of these ($\lambda = 3916{\cdot}26$, $\nu = 25527{\cdot}3$) belongs to class I., but Catalan has not found that it has any connection with the multiplet, although he includes it in the list of the lines given in Table LIX.

The structure of the third multiplet is as follows :—

				22859·9	116·6	22976·5	59·9	23036·4
				71·3		71·4		
		22763·4	167·8	22931·2	116·7	23047·9		
		106·7		106·7				
22657·7	212·4	22870·1	167·8	23073·9				
141·0		141·0						
22798·7	212·4	23011·1						
173·8								
22972·5								

An important result of this advance made by Catalan is that it affords undoubted evidence that the individual spectral terms in the case of manganese and chromium are more complex than in the cases already dealt with in which the maximum complexity was found to be three-fold. The most complex structure hitherto considered is that of the diffuse triplets of the alkaline earth metals formed by the combination of three-fold *p*- and *d*-terms, as already described and explained by Sommerfeld with his conception of inner atomic numbers.

Catalan's discovery of still greater multiplicities has enabled Sommerfeld not only to allocate the manganese multiplets to their respective series, but also to extend and identify the inner quantum numbers.[1] Before we deal with further experimental work which has been done on the multiplets and series relations of other elements, it is advisable for our better understanding of this work first to consider Sommerfeld's extension of his inner atomic number conception and also Landé's valuable contributions to this very fascinating extension of the simple series relationships which we have already reviewed. To this may also be added an account of the most recent experimental work on the intensities of the lines composing the multiplets. This will then permit us to take cognisance of later work on the multiplets occurring in the spectra of other elements.

[1] *Ann. der Phys.*, **70**, 32 (1923).

The Physical Basis of the Inner Quantum Number.—In order to follow Sommerfeld's next step we may first restate the general theory.[1] In order to define any individual spectrum line it is necessary to invoke three quantum numbers, namely (1) the azimuthal quantum number k; (2) the principal or total quantum number n, and (3) the inner quantum number i. It is now customary to use the total quantum number as the result of Bohr's later work referred to on p. 107, the orbit being defined by the general symbol n_k. The azimuthal quantum number determines the type of the series to which the line belongs (principal, sharp, diffuse, etc), the principal quantum number determines the order number of the line within its series, whilst the inner quantum number differentiates between the various energy levels associated with a single spectral term (singlet, doublet, triplet, etc.) This theory was applied above with great success to the simple cases of the doublet and triplet series of the alkali and alkaline earth metals.

As was previously mentioned, as far as the physical meaning of the inner quantum number is concerned, this was somewhat empirical, and the same can be said of the selection principle as applied to this quantum number, namely that only those transitions are possible in which $\Delta i = 0$ or ± 1. After the original paper was published, considerable advance was made by Landé and by Heisenberg, whose work will be more extensively described under the Zeeman effect. It has been shown that the inner quantum number multiplied by $h/2\pi$ gives the total moment of momentum of the atom in the particular state of excitation (or at any rate is very closely associated with it). That being so it is easy to see that the restriction in the transitions of the inner quantum number has a theoretical basis, since Rubinowicz has shown that in any change associated with energy radiation the total moment of momentum of an atom can only change by $\pm h/2\pi$ or zero.

Catalan's investigation of the spectrum of manganese was described in some detail above, where it was shown that he found a principal series and a sharp series, each of which consists of simple triplets. We may conclude from this that, as in the case of the alkaline earth metals, the s-term is simple and the p-term is three-fold, and for the present assign to these, as previously, the inner quantum numbers 1 and 2, 1, 0, respectively.

On the other hand, the diffuse triplet $2p - 3d$ does not consist of six lines, as in the case of the alkaline earth metals, but of nine lines, and the structure of this was explained by the combination of a three-fold p-term with a five-fold d-term. The wave-numbers of the lines can be assigned to the transitions as follows :—

i.	3.		2.		1.		0.		$\bar{1}$.
	d_1.	Δd.	d_2.	Δd.	d_3.	Δd.	d_4.	Δd.	d_5.
2 p_1	28007·16	2·34	28004·82	1·85	28002·97				
Δp			173·70		173·71				
1 p_2			28178·52	1·84	28176·68	1·24	28175·44		
Δp					129·17		129·14		
0 p_3					28305·85	1·27	28304·58	0·90	28303·68

[1] *Ann. der Phys.*, **70**, 32 (1923).

Each of the nine wave-numbers is the result of the combination of the p-term on the left with the d-term above it. As can be seen $p_1 < p_2 < p_3$, and $d_1 < d_2 < d_3 < d_4 < d_5$. The same inner quantum numbers as before, 2, 1, 0, have been assigned to the p-terms, and to the d-terms the inner quantum numbers 3, 2, 1, 0, $\bar{1}$. The formal use of a negative quantum number is adopted for the moment, because these values give the nine lines by combinations which do not transgress the selection principle. The only point to be noted is that the transition $0 \rightarrow 0$, which was previously found to be specially forbidden, seems here to occur. This divergence from previous experience, together with the negative value of i, indicates the necessity of a correction of the inner quantum numbers as regards their absolute values. At the moment there is not enough information at our disposal to enable us to do this, and consequently we may provisionally leave these values as they are.

A method of indicating the combinations is shown in Fig. 8, in which the combinations occurring in the case of the alkaline earth metals are shown to the left of the dotted line.

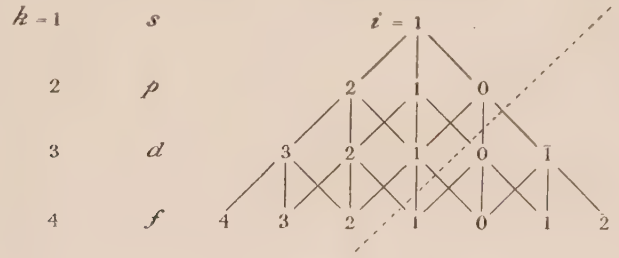

FIG. 8.

In view of the magnitude of the differences $p_1 - p_2$ and $p_2 - p_3$ compared with the four d-differences, the grouping of the lines as $3 + 3 + 3$ at once strikes the eye, but it is also possible to group the lines according to the particular d-term to which they belong. From this point of view the structure of the complex triplet is given by $1 + 2 + 3 + 2 + 1$. In Fig. 8 is also shown the probable construction of the combination $3d - - nf$, for it seems justifiable to assume that the fundamental term is seven-fold. As can be seen this member of the fundamental series should consist of $1 + 2 + 3 + 3 + 3 + 2 + 1 = 15$ lines.

Some information is gained from a consideration of the intensities of the constituent lines of the (pd) combination which for the given inner quantum number transitions are as follows :—

p	2			1			0		
d	3	2	1	2	1	0	1	0	$\bar{1}$
Intensity	10	9	7	8·5	8	7·5	7·5	8	8

In the first triplet the intensities obey the rule enunciated by Sommerfeld and given above on p. 114, the lines of the second triplet also obey the rule but less satisfactorily, whilst in the third triplet the rule is contradicted. This again emphasises the necessity of the correction of the inner quantum numbers, since the rule is rigidly obeyed in the triplets of the alkaline earth metals.

We may next turn to the intercombination lines observed by Catalan and first consider the simple S-term which enters into the combinations—

Strongest line . .	$1S - 2p_2$,	$\lambda = 5394{\cdot}7$
Weaker line . .	$1S - 2p_3$,	$\lambda = 5432{\cdot}6$,

the line $1S - 2p_1$ being absent. It may be presumed from this that the same is true of manganese as of the alkaline earth metals, and that the inner quantum numbers undergo the following transitions :—

$$\begin{array}{lll} k = 1 & S & i = 0 \\ & & \diagup\,\vert \\ 2 & p & 2 \quad 1 \quad 0 \end{array}$$

Once again, therefore, the necessity for correction becomes obvious in order to explain why the transition expressed by $0 \rightarrow 0$ is possible in the case of manganese.

Catalan shows that the combination 1S — 2P, which gives single lines with the alkaline earth metals, gives a triplet with manganese. The P-term therefore is three-fold and we must necessarily give these three terms the inner quantum numbers 1, 0, $\bar{1}$, respectively, since all three combine with 1S for which $i = 0$. If we did not do this the selection principle would be disobeyed.

The triplet at $\lambda = 4034{\cdot}5$, $4033{\cdot}1$, $4030{\cdot}8$, observed by Catalan, Sommerfeld allocated to another principal series $1S - 2P_i'$, and since once again all three lines occur, he allocated to the three-fold term P_i' the same inner quantum numbers as to P_i, namely 1, 0, $\bar{1}$.

These two three-fold terms P_i and P_i' combine with certain five-fold terms which may be indicated by D. Each resulting multiplet consists of nine lines and this is analogous to those given by the combination $(p_i d_i)$. Now we have assigned the inner quantum numbers 1, 0, $\bar{1}$ to the P_i and P_i' terms, and in order to explain the formation of nine lines it is necessary to assign to the five-fold D-terms the inner quantum numbers 2, 1, 0, $\bar{1}$, $\bar{2}$. We then obtain the transitions shown in Fig. 9,

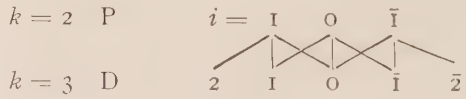

Fig. 9.

and in this way only can nine lines be formed without contravening the selection principle.

Six multiplets of the type PD were noted by Catalan. In the following table D and D′ are two five-fold terms having the differences

D′,	$\Delta\nu =$	4·8	3·5	2·6	1·4
D,	$\Delta\nu =$	229·7	169·6	116·9	68·6

P″ and P‴ are two new triplet terms :—

	Combination.	
$\lambda = 4455$	to 4462	P′D′
$\lambda = 8740$	,, 8671	PD′
$\lambda = 5341$	,, 5538	DP
$\lambda = 12990$	,, 13997	DP′
$\lambda = 3578$	,, 3630	DP″
$\lambda = 3044$	,, 3082	DP‴

The significance of the symbols DP is that the D-term is greater than the P-term, the opposite being the case with the combination represented by PD. Between the D- and D′-terms on the one hand and the *d*-terms on the other hand there is a remarkable difference. The *d*-levels are arranged in the usual way, the uppermost level having the largest inner quantum number. The D and D′ are arranged in the reversed order, since the lowest level must have the largest inner quantum in order that the selection principle be not contravened. This is sufficiently indicated by the scheme of levels shown in Fig. 10. In order to differentiate between the two types we may speak of them as regular and reversed terms respectively.

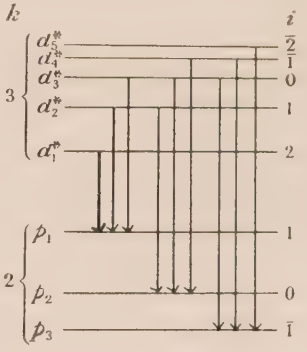

Fig. 10.

This differentiation is by no means an arbitrary one, because the differences between the levels (ΔD) decrease with decreasing values of i in both types. It is therefore possible to determine whether a term is regular or reversed by arranging the members of that term in a series with decreasing values of ΔD. In a regular term the absolute values of the members increase in that series, whilst in a reversed term the absolute values decrease. In addition to the D- and D′-terms, the P″- and P‴-terms are also reversed.

We have now finally to consider the (DD′) and the (DF) multiplets. In the case of the former we have already fixed the inner quantum numbers and consequently can at once write down the transitions as in Fig. 11.

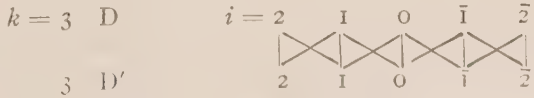

Fig. 11.

The multiplet therefore consists of thirteen lines. Catalan recognised two groups of this type which according to Sommerfeld are given by the combinations (DD'') and (DD'''), where D'' and D''' are two new, reversed, five-fold terms. The values of ΔD'' and ΔD''' were given previously on p. 129 and need not be repeated here.

The most complicated multiplet observed by Catalan was the one between $\lambda = 3844$ and 3777 containing fifteen lines. He considered that this multiplet is given by the combination of a five-fold and a seven-fold term, the former being the previously recognised D-term. It is obvious that this is not of the (DD') type owing to the number of lines and consequently it must be a (DF) type, since the selection principle restricts the transition in the azimuthal quantum number to $\Delta k = \pm 1$ and it is unthinkable that there should exist a seven-fold P term. The inner quantum numbers of the D-term being fixed, we must attribute the lines to the transitions shown in Fig. 12.

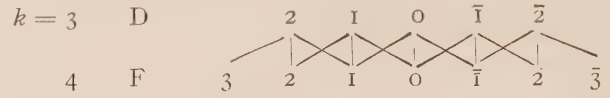

FIG. 12.

It may be pointed out that the differences between the successive members of the F-term,

$$\Delta F = 115{\cdot}3 \quad 95{\cdot}5 \quad 71{\cdot}4 \quad 49{\cdot}0 \quad 28{\cdot}5 \quad 9{\cdot}8,$$

are abnormally large for a fundamental term.

The fact that the spark spectrum of manganese also shows multiplets of the type (PD) and that Mn and Mn^+ exhibit similar spectra in contravention of the law of spectroscopic displacement Sommerfeld attributed to the position of this element in the periodic table. The spectroscopic displacement law at the same time offers an explanation of the analogy between the spectra of chromium and ionised manganese, which is evidenced by the chromium multiplet of the (PD) type observed by Catalan at $\lambda = 5300$. There is also an analogy in the chromium multiplets at $\lambda = 3900$ and $\lambda = 4350$. Sommerfeld attributed these multiplets to the (DD') and (DF) types because the reversed chromium terms have a closer resemblance to the D-, D'-, and F-terms of manganese than they have to the *d*-, *d'*-, and *f*-terms. Now the chromium multiplet (DD') at $\lambda = 3900$ contains only eleven lines, whereas the corresponding manganese multiplet contains thirteen lines. Catalan, however, points out that a twelfth line ($\lambda = 3916{\cdot}26$) may well belong to the multiplet owing to its general resemblance to the others. Sommerfeld then includes this line and asks why the chromium multiplet contains only twelve as against thirteen in the case of manganese. He says that clearly this is due to the fact that Landé's special restriction holds good, namely, that the inner quantum number transition $0 \rightarrow 0$ is forbidden. He therefore assigns the inner quantum numbers as follows :—

i.		4.		3.		2.		1		0.
		D_1'.		D_2'.		D_3'.		D_4'.		D_5'.
4	D_1	25508·4	144·6	25363·8						
	D	212·6		212·6						
3	D_2	25721·0	144·4	25576·4	129·7	25446·7				
				167·4		168·1				
2	D_3			25743·8	129·0	25614·8	118·7	25496·1		
						116·6		117·2		
1	D_4					25731·4	118·1	25613·3	86·0	25527·3
								59·7		
0	D_5							25673·0		

He thus in the case of chromium was able to fix the inner quantum numbers, and the transitions are shown in Fig. 13.

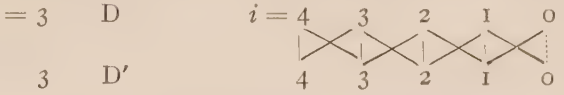

FIG. 13.

The $0 \rightarrow 0$ transition is dotted in order to show that it is unreal. If the transition did take place the wave-number of the resulting line would be of course

$$25673{\cdot}0 - 86{\cdot}0 = 25527{\cdot}3 + 59{\cdot}7 = 25587{\cdot}0.$$

We can now find an explanation of the structure of the chromium multiplet at $\lambda = 4350$ which is a combination of the five-fold D-term given in the above table and an F-term. The multiplet contains twelve lines due to the transition shown in Fig. 14.

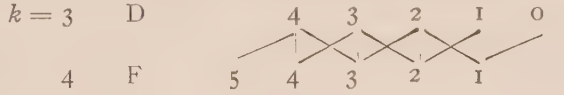

FIG. 14.

The Absolute Values of the Inner Quantum Numbers. Sommerfeld, in his third paper,[1] agrees with Landé and with Bohr that the physical significance of the inner quantum number i is to be found in the fact that $ih/2\pi$ is the total moment of momentum of the atom. Further, the total moment of momentum is the vector sum of the moment i_s of the s-state and the moment i_a of the excitation.

If now r be the permanent number of levels on any system, then we have, generally,

$$r = 2i_s + 1,$$

where i_s in fact is the inner quantum number of the sharp term, which is always single and has $k = 1$. The statement at the beginning of the section as to the increase in the number of levels as k increases can be expressed as follows :—

[1] *Ann. der Phys.*, **73**, 209 (1924).

If we put $i_a = k - 1$,
then $$i_{max} = i_s + i_a,$$
and $$i_{min} = | i_s - i_a | = \begin{cases} i_s - i_a \text{ when } i_s > i_a \\ 0 \quad \text{when } i_s = i_a \\ i_a - 1_s \text{ when } i_s < i_a \end{cases}$$

where i_{max} and i_{min} are the maximum and minimum values of i for any given term.

Applying this to systems with uneven multiplicities we obtain the scheme for singlet, triplet, quintet, and septet systems as shown in Fig. 15. The links indicate the possible combinations.

The vector summation of i_s and i_a may be indicated by a geometrical construction which leads also to the scheme shown in Fig. 15. This may be done for the septet system where $i_s = 3$, and $i_a = 1, 2, 3$, and 4 for the *p*-, *d*-, *f*-, and *g*-levels.

On the vertical straight line in Fig. 16 is marked off the length 03 to represent the integral value 3 of i_s. Then with centre 3 and radii $i_a = 1, 2, 3$, and 4, the four full semi-circles *p*, *d*, *f*, and *g* are drawn. Then with centre 0 and radii $i_a = 1, 2, 3$, etc., the dotted arcs 1, 2, 3, etc., are drawn as shown. Inasmuch as the values of i are integral the intersections of the dotted arcs with each full semi-circle represent the end points of the vector sums, i, for that particular level. The vector sums are not shown in the figure and would be given by straight lines drawn from the point 0 to the various points of intersection of the full and dotted arcs. In order to indicate this, one such vector sum is indicated by the straight line from 0 to d_4. When we consider the individual groups of levels we have on the *p*-level only three vector sums or inner quantum numbers, namely, $i = 2$, 3, and 4. On the *d*-level we have five, namely, $i = 1, 2, 3, 4, 5$, whilst on the *f*- and *g*-levels we have seven, namely, $i = 0, 1, 2, 3, 4, 5, 6$, and $i = 1, 2, 3, 4, 5, 6, 7$, respectively. These are the same as shown in Fig. 15 above.

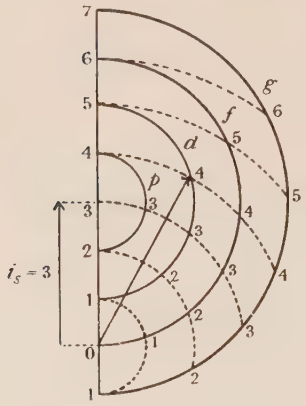

FIG. 16.

In his earlier paper Sommerfeld attempted to correct the inner quantum numbers which he provisionally assigned to the levels of the manganese terms in the belief that the terms were five-fold and seven-fold. More recent work, however, to be mentioned below, has shown that the multiplicities are even in the case of the spectrum of neutral manganese and consequently we need not follow Sommerfeld's earlier discussion of the manganese multiplets any further.

It is quite obvious of course that even multiplicities must exist,

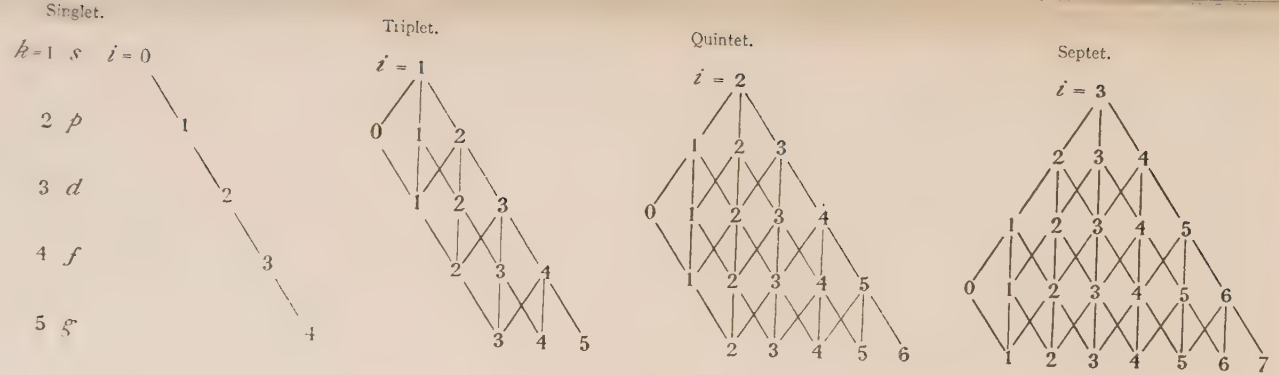
Singlet.
Triplet.
Quintet.
Septet.
k = 1 s i = 0
2 p
3 d
4 f
5 g
i = 1
i = 2
i = 3

FIG. 15.

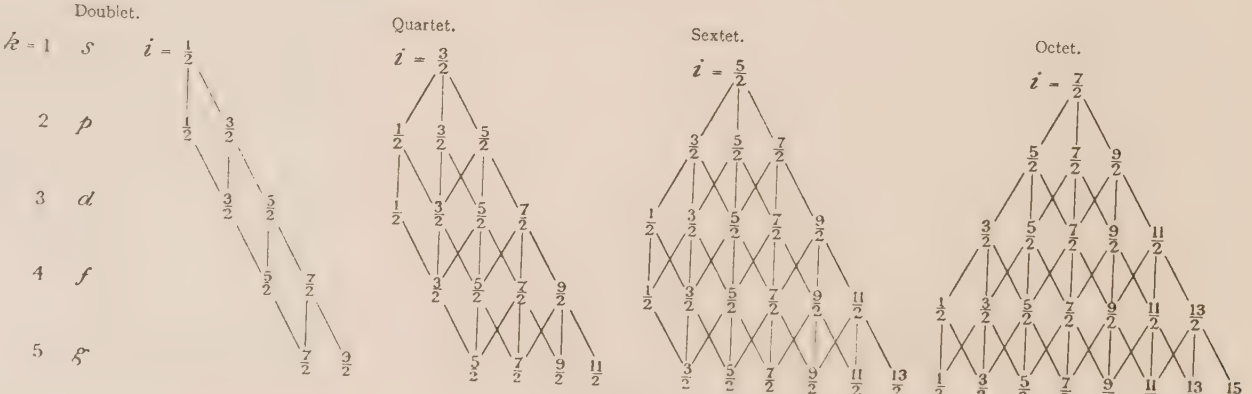
Doublet.
Quartet.
Sextet.
Octet.
k = 1 s
2 p
3 d
4 f
5 g
i = 1/2
i = 3/2
i = 5/2
i = 7/2

FIG. 17.

since we have the evidence of the doublet systems of the alkali metals, and these cannot be fitted in with the scheme shown in Fig. 15. The later work to which I have referred, based on the Zeeman effect, has proved that in addition to the doublet systems of the alkali metals there also exist quartet, sextet, and octet systems. Now Sommerfeld in his earlier paper pointed out that these even terms can only be explained by the use of half-quantum numbers and he gave a provisional scheme. This was to some extent modified in his last paper and also explained in the last edition of his book.[1]

An important feature of these systems in which the permanent value of multiplicities is even ($r = 2, 4, 6$ or 8) is that as k increases the number of levels increases in the uneven series 1, 3, 5, . . . $r - 1$ and then becomes even. This can at once be seen from the simplest case of the doublet system which begins with the simple s-term (uneven) and reaches the permanent value of 2 in the p-term. Sommerfeld explains this by giving half-quantum values to the inner quantum number i and to the quantum number i_s. Since we have the relation

$$i_a = k - 1,$$

the values of i_a must be integral. He arrives then at the scheme shown in Fig. 17, the connecting links again showing the possible combinations.

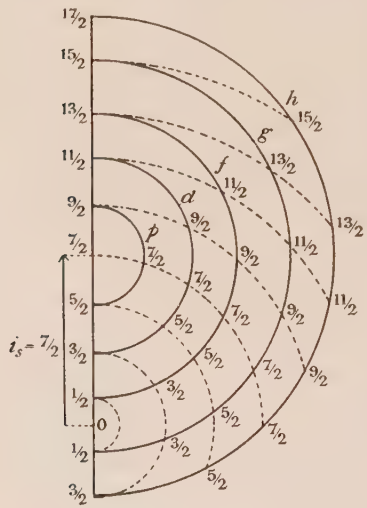

FIG. 18.

The geometrical construction which leads to this scheme is shown in Fig. 18 for the octet system. In this case $i_s = 7/2$ and $i_a = 1, 2, 3, 4$, etc., for the p, d, f, g, etc., levels. On the vertical straight line the distance $i_s = 7/2$ is marked out and with centre $7/2$ and radii 1, 2, 3, etc., are drawn the full semi-circles which represent the p, d, f, etc., levels. On these semi-circles we have to find all the half-integral points, and in order so to do the dotted arcs are drawn with centre 0 and radii $1/2$, $3/2$, $5/2$, etc., and the intersections of these dotted arcs with each full semi-circle give the ends of the half-integral vector sums or inner quantum numbers for that level. For the p-term we have therefore $5/2$, $7/2$, and $9/2$, for the d-term $3/2$, $5/2$, $7/2$, $9/2$, $11/2$, for the f-term $1/2$, $3/2$, $5/2$, $7/2$, $9/2$, $11/2$, $13/2$, and for the g-term $1/2$, $3/2$, $5/2$, $7/2$, $9/2$, $11/2$, $13/2$, $15/2$. These values are the same as those given in Fig. 17 and we can now understand why it is that in

[1] *Ann. der Phys.*, **73**, 209 (1924); *Atombau und Spektrallinien*, p. 590.

systems of even multiplicities the number of terms first of all increases with k in the series 1, 3, 5, . . . $r - 1$ and then becomes equal to r and remains constant. This is shown in Fig. 18 by the h-term which like the g-term has eight levels with the inner quantum numbers 3/2, 5/2, 7/2, 9/2, 11/2, 13/2, 15/2, 17/2. This may be expressed by the following general rule: In systems with even values of permanent multiplicities the number of levels first increases in the odd series 1, 3, 5, etc., until the value $i_{\min} = 1/2$ is reached. The next level has also $i_{\min} = 1/2$, but the number of levels is now increased by unity and becomes even and constant.

There is no doubt that the use of the half-quantum numbers presents some difficulty from the purely theoretical point of view, but it is not possible to enter into this question here. Their adoption has been forced on us not only by the phenomena under discussion at the moment, but more strongly still by the phenomena of band spectra which will be discussed in Chapter IV.

In actual practice the use of half-quantum numbers in descriptive writing or printing is very far from being convenient, and it is customary to adopt the convention of expressing Sommerfeld's inner quantum numbers of systems of even multiplicities, not as the half-integral numbers i, but as $i + 1/2$. The adoption of this convention commits us to nothing, for the essential fact of the unit difference between any two consecutive inner quantum numbers is still maintained, and it does not modify in any way the restrictions laid down by the selection principle. This convention will again be referred to in discussing Landé's work.

In connection with nomenclature there is one point which may be mentioned here, namely, the difference between the identification of a specific term level by its inner quantum number and the older method used in the literature of spectral series. This difference may be illustrated by the case of the D-lines of sodium which according to the older method were indicated by

$$\begin{aligned} D_2 \quad & \lambda = 5890, \qquad 1\sigma - 2\pi_1 \\ D_1 \quad & \lambda = 5896, \qquad 1\sigma - 2\pi_2, \end{aligned}$$

where of course $\pi_1 < \pi_2$ and hence the use of the subscript numbers. On the other hand (expect in reversed terms), the lowest level or largest term has the smallest inner quantum number and consequently, if the subscripts mean inner quantum numbers, then we have

$$\begin{aligned} D_2 \quad & \lambda = 5890, \qquad 1\sigma - 2\pi_2 \\ D_1 \quad & \lambda = 5896, \qquad 1\sigma - 2\pi_1. \end{aligned}$$

In view of the significance of the inner quantum numbers it has now been accepted by many that the designation of a spectral term shall be based on its inner quantum number. It is possible that were it not for this timely warning the unwary might be puzzled by an apparently gratuitous reversal in the order of enumeration of the different levels associated with a given azimuthal quantum number.

Reference has been made more than once to Landé in the foregoing, and it is to him that we owe a great debt for his work on the theory of the Zeeman effect. A knowledge of the structure of multiplets, both simple and complex, is essential in studying their magnetic resolution and this knowledge has been not a little advanced by him. It is necessary for us here to mention Landé's work in the present connection in order that its application to the Zeeman effect may be understood when we discuss this phenomenon.[1]

Landé defines the spectral term in a somewhat different way from Sommerfeld. He takes the azimuthal moment of momentum $kh/2\pi$, the moment of momentum of the atomic trunk $rh/2\pi$, and their vector sum, or total moment of momentum, $ih/2\pi$, where of course k is the azimuthal quantum number and i is the inner quantum number of Sommerfeld. The values of k, r, and i are integral and $r = 1, 2, 3$, etc., for singlet, doublet, triplet, etc., terms. Landé shows that there are many reasons for giving to the quantum numbers r and k not integral but half-integral values. He therefore assigns to the series s, p, d, etc., not the integral azimuthal quantum number of Sommerfeld, $k = 1, 2, 3$, etc., but the half-integral values $K = 1/2, 3/2, 5/2$, etc. Landé's azimuthal quantum numbers K are therefore throughout smaller than Sommerfeld's by $1/2$. Similarly in place of $r = 1, 2, 3$, etc., he puts $R = 1/2, 2/2, 3/2$, etc., and for the vector sums of the two moments of momentum he obtains $I = 1/2, 3/2, 5/2$, etc., for uneven multiplicities and $I = 2/2, 4/2, 6/2$, etc., for even multiplicities. As may be seen, therefore, Landé's values for the inner quantum numbers are throughout greater than Sommerfeld's by $1/2$. The vector summation of R and K may be shown geometrically in exactly the same way as in Fig. 16 and 18.

The adoption by Landé of these different values for r, k, and i makes no modification necessary in what was stated previously in connection with the selection principle, except in one particular. The special prohibition of the transition $0 \rightarrow 0$ in the inner quantum number becomes the special prohibition of the transition $I \rightarrow I = 1/2 \rightarrow 1/2$.

It will be seen that Landé and Sommerfeld do not agree as to the absolute values of the inner quantum numbers, and indeed Bohr has come to the conclusion that the values are greater than those of Sommerfeld throughout by unity. In all three scales of enumeration the essential feature is maintained of unit difference between the inner quantum numbers of any two consecutive energy levels of any single term.

It must be pointed out that Landé arrives at exactly the same schemes for the number of levels peculiar to the various terms in the

[1] A. Landé, *Preuss. Akad. Wiss. Ber.* (1919), 101; *Phys. Zeitsch.*, **20**, 228 (1919); *Deutsch. phys. Ges. Verh.*, **21**, 585 (1919); *Phys. Zeitsch.*, **22**, 417 (1921); *Zeitsch. für Phys.*, **15**, 189 (1923); **17**, 292 (1923); *Phys. Zeitschr.*, **24**, 441 (1923); *Zeitsch. für Phys.*, **25**, 46 (1924). See also *Zeemaneffekt und Multiplettstruktur der Spektrallinien*, E. Back and A. Landé, Julius Springer, Berlin, 1925.

odd and even systems as Sommerfeld and as was shown in Figs. 15 and 17. The same inconvenience in writing and printing the half-integral quantum numbers is found in Landé's scheme as was previously referred to in the case of that of Sommerfeld. The inconvenience however occurs in the former in connection with terms of the uneven system of multiplicities. Landé adopts the convention of expressing the values of I for the even systems as $i = I - 1/2$, leaving the integral values for the uneven systems (2/2, 4/2, 6/2, etc.) unchanged. As the result of this convention and that adopted previously, Landé and Sommerfeld agree in the values used in writing and printing the inner quantum numbers. It must be noted that on this convention the minimum value of i is 0 in uneven systems and 1 in even systems of multiplicities.

It can be seen from the foregoing that any spectral term is characterised by four quantum numbers n, r, k, and i, where n is the number of the term in the appropriate series. Indeed a given term can at once be defined by the values of n, r, k, and i, and Landé in agreement with Paschen expresses a spectral term by the symbol

$$n^r_{ki},$$

and in so doing he uses the integral values of r and k employed by Sommerfeld and the conventional values of i. It will be remembered that $r = 1, 2, 3$, etc., for singlet, doublet, triplet, etc., systems. In order to illustrate the use of this symbolic method the old spectral series designations together with the new symbols are given in Table LX.

TABLE LX.

Singlet terms.			Doublet terms.					Triplet terms.						
Old	nS	nP	nD	$n\sigma$	$n\pi_2$	$n\pi_1$	$n\delta_2$	$n\delta_1$	ns	np_3	np_2	np_1	nd_3	nd_2	nd_1
New	n^1_{10}	n^1_{21}	n^1_{31}	n^2_{11}	n^2_{21}	n^2_{22}	n^2_{32}	n^2_{33}	n^3_{11}	n^3_{20}	n^3_{21}	n^3_{22}	n^3_{31}	n^3_{32}	n^3_{33}

There is no question but that this symbolic method is extremely convenient and it has generally been adopted in German literature. I propose to adopt it in describing the more recent work on the multiplets of chromium and iron. Attention may again be drawn to the reversal in the order of the subscripts of the terms when the inner quantum numbers are used. The combination of the two terms to give a spectrum line may be illustrated by the D-lines of sodium which are expressed as follows :—

$$D_2 \quad \lambda = 5890 \qquad I^2_{11} - 2^2_{22}$$
$$D_1 \quad \lambda = 5896 \qquad I^2_{11} - 2^2_{21}.$$

The whole scheme of multiple terms is shown in Table LXI. with the new symbols.

TABLE LXI.

Uneven multiplicities.									Even multiplicities.								
$I = \frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$	$\frac{9}{2}$	$\frac{11}{2}$	$\frac{13}{2}$	$\frac{15}{2}$		$\frac{2}{2}$	$\frac{4}{2}$	$\frac{6}{2}$	$\frac{8}{2}$	$\frac{10}{2}$	$\frac{12}{2}$	$\frac{14}{2}$	$\frac{16}{2} = I$	
k $i = 0$	1	2	3	4	5	6	7		1	2	3	4	5	6	7	$8 = i$	K
1 n^1_{10}					Singlet terms, $r = 1$ $R = \frac{1}{2}$				n^2_{11}				Doublet terms, $r = 2$ $R = \frac{2}{2}$				s $\frac{1}{2}$
2	n^1_{21}								n^2_{21}	n^2_{22}							p $\frac{3}{2}$
3		n^1_{32}								n^2_{32}	n^2_{33}						d $\frac{5}{2}$
4			n^1_{43}								n^2_{43}	n^2_{44}					f $\frac{7}{2}$
1	n^3_{11}				Triplet terms, $r = 3$ $R = \frac{3}{2}$					n^4_{12}			Quartet terms, $r = 4$ $R = \frac{4}{2}$				s $\frac{1}{2}$
2 n^3_{20}	n^3_{21}	n^3_{22}							n^4_{21}	n^4_{22}	n^4_{23}						p $\frac{3}{2}$
3	n^3_{31}	n^3_{32}	n^3_{33}						n^4_{31}	n^4_{32}	n^4_{33}	n^4_{34}					d $\frac{5}{2}$
4		n^3_{42}	n^3_{43}	n^3_{44}						n^4_{42}	n^4_{43}	n^4_{44}	n^4_{45}				f $\frac{7}{2}$
1		n^5_{12}			Quintet terms, $r = 5$ $R = \frac{5}{2}$						n^6_{13}			Sextet terms, $r = 6$ $R = \frac{6}{2}$			s $\frac{1}{2}$
2	n^5_{21}	n^5_{22}	n^5_{23}							n^6_{22}	n^6_{23}	n^6_{24}					p $\frac{3}{2}$
3 n^5_{30}	n^5_{31}	n^5_{32}	n^5_{33}	n^5_{34}					n^6_{31}	n^6_{32}	n^6_{33}	n^6_{34}	n^6_{35}				d $\frac{5}{2}$
4	n^5_{41}	n^5_{42}	n^5_{43}	n^5_{44}	n^5_{45}				n^6_{41}	n^6_{42}	n^6_{43}	n^6_{44}	n^6_{45}	n^6_{46}			f $\frac{7}{2}$
1			n^7_{13}		Septet terms, $r = 7$ $R = \frac{7}{2}$						n^8_{14}		Octet terms, $r = 8$ $R = \frac{8}{2}$				s $\frac{1}{2}$
2		n^7_{22}	n^7_{23}	n^7_{24}						n^8_{23}	n^8_{24}	n^8_{25}					p $\frac{3}{2}$
3	n^7_{31}	n^7_{32}	n^7_{33}	n^7_{34}	n^7_{35}				n^8_{32}	n^8_{33}	n^8_{34}	n^8_{35}	n^8_{36}				d $\frac{5}{2}$
4 n^7_{40}	n^7_{41}	n^7_{42}	n^7_{43}	n^7_{44}	n^7_{45}	n^7_{46}			n^8_{41}	n^8_{42}	n^8_{43}	n^8_{44}	n^8_{45}	n^8_{46}	n^8_{47}		f $\frac{7}{2}$
5	n^7_{51}	n^7_{52}	n^7_{53}	n^7_{54}	n^7_{55}	n^7_{56}	n^7_{57}		n^8_{51}	n^8_{52}	n^8_{53}	n^8_{54}	n^8_{55}	n^8_{56}	n^8_{57}	n^8_{58}	g $\frac{9}{2}$
$\Delta\nu =$ 1 : 2 : 3 : 4 : 5 : 6 : 7									$\frac{3}{2} : \frac{5}{2} : \frac{7}{2} : \frac{9}{2} : \frac{11}{2} : \frac{13}{2} : \frac{15}{2} = \Delta\nu$								

A strong argument in favour of the use of the half-integral values K, R, and I is to be found in Landé's law of the wave-number differences between any two terms n^r_{ki} and $n^r_{ki'}$, that is to say, any two terms which differ only in their inner quantum numbers. If it be assumed that the force of attraction between the electron and the atomic trunk has its origin in a potential energy which is proportional to cos (R, K), then the various members of a multiple term will only differ by an amount which is proportional to

$$\cos(\mathrm{R}, \mathrm{K}) = \frac{\mathrm{I}^2 - \mathrm{K}^2 - \mathrm{R}^2}{2\mathrm{RK}}.$$

The wave-number difference of two members of the same multiple term (that is to say, with equal values of R and K) will be proportional to

$$\frac{\mathrm{I}^2 - \mathrm{I}'^2}{2} = \frac{\mathrm{I} + \mathrm{I}'}{2}(\mathrm{I} - \mathrm{I}').$$

It follows therefore that the wave-number difference between two consecutive levels of a multiple term, when of course $\mathrm{I} - \mathrm{I}' = 1$, will be proportional to $\frac{\mathrm{I} + \mathrm{I}'}{2}$. Using the values of I given in the top row of Table LXI. of the multiple terms we find that the intervals between the consecutive levels of the multiple terms are proportional to

$$\Delta = 1 : 2 : 3 : 4 : 5 \ldots, \quad \text{and} \quad \Delta\nu = \tfrac{3}{2} : \tfrac{5}{2} : \tfrac{7}{2} : \tfrac{9}{2} : \tfrac{11}{2} \ldots$$

Uneven multiplicities. Even multiplicities.

These relative values of the wave-number intervals are given in the bottom row of Table LXI.

This law has been verified in a number of instances, and one example of its validity has of course long been known in the case of a triplet term where $\Delta\nu_1$ is always equal to $2\Delta\nu_2$. Deviations from this law indicate that the potential energy is not exactly proportional to cos (R, K), but that this is a close approximation. In spite of this it may be said that the law justifies the use of the half-integral values for R, K, and I, and furthermore the law gives very material assistance in elucidating the structure of multiplets as will presently be shown.

Reference was made previously to the fact that the early conclusions drawn by Catalan and by Sommerfeld from the multiplets of neutral manganese, namely, that the terms are of uneven multiplicities (quintet and septet), have more recently been shown to be incorrect. This new work was carried out by Back [1] who succeeded in proving from observations of the Zeeman effect and also from Landé's law of the interval ratios that the terms belong to the system of even multiplicities. As will be shown in Chap. II., the multiplicity of the terms, the combination of which gives rise to a spectrum line, can definitely be determined from the Zeeman pattern. Back was able

[1] *Zeitsch. für Phys.*, **15**, 206 (1923).

to establish beyond all doubt that the spectral terms functioning in the arc spectrum of manganese are not five-fold and seven-fold, but four-fold, six-fold, and eight-fold. This finds confirmation in the interval ratios between the consecutive term levels. It is not possible here to do more than give a brief account of Back's results.

Back does not give the Zeeman resolution of all the triplets and multiplets discovered by Catalan, but only a few which, however, are amply sufficient for the determination of the order of the multiplicities of the terms. In the arc spectrum of manganese he examined the following members :—

I.

The Sharp Triplet.

λ.	ν.	Δν.	Catalan's Designation.
4823·522	20725·96		$1s - 1p_1$
4783·432	20899·67	173·71	$1s - 1p_2$
4754·048	21028·85	129·18	$1s - 1p_3$.

The Zeeman resolution shows that this triplet belongs to an octet system and that the three lines are due to the combinations

$$n^8_{14} - n^8_{2i}, \quad \text{where } i = 3, 4, 5.$$

We have therefore $n^8_{24} - n^8_{25} = 173{\cdot}71 \text{ cm.}^{-1}$

$$n^8_{23} - n^8_{24} = 129{\cdot}18 \text{ cm.}^{-1}.$$

The interval ratio is $129{\cdot}18 : 173{\cdot}71 = 7{\cdot}2 : 9$, and the theoretical value $= 7 : 9$.

II.

The Two Parallel Systems of Narrow Triplets.

λ.	ν.	Δν.	Catalan's Designation.
4030·760	24802·83		$1S - (1P_1 + C)$
4033·074	24788·01	14·22	$1S - (1P_2 + C)$
4034·489	24779·31	8·70	$1S - (1P_3 + C)$
2794·822	35769·94		$1S - 1P_1$
2798·273	35725·82	44·12	$1S - 1P_2$
2801·076	35690·07	35·75	$1S - 1P_3$

$$C = 109671{\cdot}71.$$

Both these triplets give Zeeman resolutions which unmistakably conform to the type belonging to the sextet system and consequently the term 1S is to be denoted by n^6_{13}. The two triplets therefore are given by the combinations

		$\Delta\nu$.
	$n^6_{13} - n^6_{24}$	14·22
	$n^6_{13} - n^6_{23}$	8·70
	$n^6_{13} - n^6_{22}$	
and	$n^6_{13} - n^6_{24a}$	44·12
	$n^6_{13} - n^6_{23a}$	35·75
	$n^6_{13} - n^6_{22a}$	

The interval ratios are therefore

$$14{\cdot}22 : 8{\cdot}70 = \begin{cases} 7 : 4{\cdot}3 \text{ obs.} \\ 7 : 5{\cdot}0 \text{ calc.} \end{cases}$$

and

$$44{\cdot}12 : 35{\cdot}75 = \begin{cases} 7 : 5{\cdot}7 \text{ obs.} \\ 7 : 5{\cdot}0 \text{ calc.} \end{cases}$$

The agreement is not all that can be desired, but as Back says it is remarkable that the mean of the observed values of the two triplets is exactly 7 : 5.

III.

TABLE LXII.

Multiplet at $\lambda = 3843{\cdot}985$.

	λ.	ν.			λ.	ν.	
I.	3776·537	26471·79	D_1F_3	IX.	3829·674	26104·50	D_4F_6
II.	3790·215	26376·19	D_1F_2	X.	3833·864	26075·92	D_4F_5
III.	3799·256	26313·49	D_2F_4	XI.	3834·363	26072·58	D_3F_3
IV.	3806·866	26260·93	D_1F_1	XII.	(3838·329)	(26045·64)	(D_5F_7)
V.	3809·599	26242·07	D_2F_3	XIII.	3839·777	26035·82	D_5F_6
VI.	3816·746	26192·93	D_3F_5	XIV.	3841·081	26026·97	D_4F_4
VII.	3823·515	26146·56	D_2F_2	XV.	3843·985	26007·31	D_5F_5
VIII.	3823·896	26143·94	D_3F_4				

In Table LXII. the fourth and eighth columns contain Sommerfeld's designation of the lines. Back was unable to observe line No. XII. under any conditions when using pure manganese, and he suggests that it is due to an impurity, possibly magnesium ($\lambda = 3838{\cdot}29$). The Zeeman resolutions of all the lines (excepting I., III., and VI., which were too faint for observation, and IV. which was not completely resolved) showed that the two spectral terms belong to a sextet system, the general expression being

$$n^6_{3i} - n^6_{4i}$$

$$i = 1, 2, 3, 4, 5; \quad i = 1, 2, 3, 4, 5, 6.$$

The absence of line XII. is therefore of great importance, since Sommerfeld explained it by assuming the fundamental term to be seven-fold. It cannot be a component of a multiplet formed by a combination of two terms of a sextet system. In Table LXIII. is shown the structure which Back assigns to this multiplet.

TABLE LXIII.

	(D_5) n^6_{31}		(D_4) n^6_{32}		(D_3) n^6_{33}		(D_2) n^6_{34}		(D_1) n^6_{35}
									10
									3806·87
$(F_1)n^6_{46}$									26260·93
									115·34
							9		3
							3823·52		3790·21
$(F_2)n^6_{45}$							26146·56	229·71	26376·27
							95·51		95·52
					8		6		1
					3834·36		3809·60		3776·54
$(F_3)n^6_{44}$					26072·58	169·49	26242·07	229·72	26471·79
					71·36		71·42		
			5		5		2		
			3841·08		3823·90		3799·26		
$(F_4)n^6_{43}$			26026·97	116·97	26143·94	169·55	26313·49		
			48·95		48·98				
	4		6		2				
	3843·99		3833·86		3816·75				
$(F_5)n^6_{42}$	26007·31	68·61	26075·92	117·00	26192·92				
	28·51		28·58						
	4		2						
	3839·78		3829·67						
$(F_6)n^6_{41}$	26035·82	68·68	26104·50						

Interval ratios ΔD, 68·65 : 117·00 : 169·57 : 229·71 = $\begin{cases} 2·7 : 4·6 : 6·6 : 9 \text{ obs.} \\ 3·0 : 5·0 : 7·0 : 9 \text{ calc.} \end{cases}$

ΔF, 28·55 : 48·96 : 71·39 : 95·51 : 115·34 = $\begin{cases} 2·8 : 4·7 : 6·8 : 9·1 : 11 \text{ obs.} \\ 3·0 : 5·0 : 7·0 : 9·0 : 11 \text{ calc.} \end{cases}$

These interval ratios entirely confirm the conclusions drawn from the Zeeman effect, since they agree quite well with the theoretical values for even spectral terms. The fact that the D-term is five-fold and the F-term is six-fold with the interval ratios shown is exactly in accordance with the general scheme of multiplicities of even terms shown in Table LXI. on p. 148. If this multiplet belonged to a septet system, there would have been thirteen lines due to the combination of a five-fold D-term with a seven-fold F-term, and the interval ratios would then be

$$\Delta D, \quad 2 : 3 : 4 : 5$$
$$\Delta F, \quad 1 : 2 : 3 : 4 : 5,$$

which in no way agree with those actually observed. The evidence in favour of the sextet system is therefore independent of the absence of the line at $\lambda = 3838·33$.

IV.

Multiplet at $\lambda = 4083{\cdot}64$ to $\lambda = 4018{\cdot}11$.

This multiplet was allocated to a (DD*) combination by Sommerfeld and this Back confirms, with however the additional proof deduced from the Zeeman effect and the interval ratios that both terms belong to the sextet system.

The general formula is $n^6_{3i} - n^{6*}_{3i}$, $i = 1, 2, 3, 4, 5$.

Interval ratios

$$\Delta\text{D}, \quad 68{\cdot}65 : 116{\cdot}96 : 169{\cdot}54 : 229{\cdot}71 = \begin{cases} 2{\cdot}7 : 4{\cdot}6 : 6{\cdot}6 : 9 \text{ obs.} \\ 3{\cdot}0 : 5{\cdot}0 : 7{\cdot}0 : 9 \text{ calc.,} \end{cases}$$

this being identical with those in the previous multiplet,

$$\Delta\text{D}^*, \quad 55{\cdot}05 : 89{\cdot}79 : 121{\cdot}10 : 143{\cdot}18 = \begin{cases} 3{\cdot}5 : 5{\cdot}6 : 7{\cdot}6 : 9 \text{ obs.} \\ 3{\cdot}0 : 5{\cdot}0 : 7{\cdot}0 : 9 \text{ calc.} \end{cases}$$

V.

Multiplet at $\lambda = 3629{\cdot}74$ to $\lambda = 3577{\cdot}80$.

Back shows again that this multiplet belongs to the sextet system and confirms the allocation by Sommerfeld to the combination (DP). The general formula is therefore

$$n^6_{3i} - n^6_{2i}$$

$$i = 1, 2, 3, 4, 5; \qquad i = 2, 3, 4.$$

Interval ratios

$$\Delta\text{D}, \quad 68{\cdot}67 : 116{\cdot}98 : 169{\cdot}53 : 229{\cdot}65 = \begin{cases} 2{\cdot}7 : 4{\cdot}6 : 6{\cdot}6 : 9 \text{ obs.} \\ 3{\cdot}0 : 5{\cdot}0 : 7{\cdot}0 : 9 \text{ calc.} \end{cases}$$

$$\Delta\text{P}, \quad 103{\cdot}07 : 162{\cdot}20 = \begin{cases} 4{\cdot}5 : 7 \text{ obs.} \\ 5{\cdot}0 : 7 \text{ calc.} \end{cases}$$

VI.

Back identified a multiplet in the manganese arc spectrum, not observed by Catalan, having the following eight lines :—

λ.	Int.	ν.	λ.	Int.	ν.
4235·125	8	23605·43	4265·920	9	23435·03
4235·306	10	23604·41	4281·097	9	23351·95
4239·723	7	23579·83	4284·084	3	23335·68
4257·653	8	23480·53	4312·546	2	23181·66

From the Zeeman resolution of all these lines Back found that this multiplet belongs to a quartet system and further that it arises from the combination (*pd*), the general formula being

$$n^4_{2i} - n^4_{3i}$$

$$i = 1, 2, 3 \qquad i = 1, 2, 3, 4.$$

The structure of this multiplet is shown in Table LXIV.

TABLE LXIV.

	n^4_{21}		n^4_{22}		n^4_{23}	
					10	
n^4_{34}					4235·31 23604·41	n^4_{34}
					252·46	
			8		9	
n^4_{33}			4325·13 23605·43	253·48	4281·10 23351·95	n^4_{33}
			170·40		170·29	
	7		9		2	
n^4_{32}	4239·72 23579·83	144·80	4265·92 23435·03	253·37	4312·55 23181·66	n^4_{32}
	99·30		99·35			
	8		3			
n^4_{31}	4257·65 23480·53	144·85	4284·08 23335·68			n^4_{31}

Interval ratios Δp, 144·83 : 253·42 = { 2·9 : 5 obs. / 3·0 : 5 calc.

Δd, 99·33 : 170·35 : 252·46 = { 2·8 : 4·8 : 7 obs. / 3·0 : 5·0 : 7 calc.

There can be no question that the results obtained by Back afford a conclusive proof that the spectral terms of the neutral manganese spectrum are of the even type, and indeed that there are three systems, quartet, sextet, and octet. This has a very great significance in view of the conclusion drawn by Sommerfeld as regards the similarity of the spectral terms of Mn and Mn^+, namely, that the Kossel and Sommerfeld law of spectroscopic displacement does not hold in the case of this element (see pp. 80 and 140). It cannot be denied that this conclusion was not very satisfactory and indeed it was only accepted provisionally until further information was available. It now becomes a matter of singular importance to determine whether the spectral terms of Mn^+ are odd or even, since, in view of the even terms of the neutral Mn spectrum, the spectroscopic displacement law demands that they should be odd.

Back has investigated the Zeeman resolution of the two triplets and two multiplets found by Catalan in the enhanced spectrum of manganese, and has succeeded in proving that the spectral terms are odd and that they belong to a quintet and a septet system. His results are as follows :—

VII.

Triplet at $\lambda = 2949{\cdot}207$, 2439·315 and 2433·066.

This is a triplet of a quintet system of which the general formula is $n^5_{12} - n^5_{2i}$, $i = 1, 2, 3$. This is confirmed by the interval ratio

$$\Delta p, \quad 72{\cdot}45 : 114{\cdot}08 = \begin{cases} 1{\cdot}9 : 3 \text{ obs.} \\ 2{\cdot}0 : 3 \text{ calc.} \end{cases}$$

Triplet at $\lambda = 2576{\cdot}116$, $2593{\cdot}734$, and $2605{\cdot}695$.

This is also a triplet due to the combination (sp) but the two terms belong to a septet system and are to be denoted by $n^7_{1_3}$ and n^7_{2i} where $i = 2, 3, 4$. This is confirmed by the interval ratio

$$\Delta p, \quad 176{\cdot}91 : 263{\cdot}58 = \begin{cases} 2{\cdot}7 : 4 \text{ obs.} \\ 3{\cdot}0 : 4 \text{ calc.} \end{cases}$$

VIII.

Multiplet at $\lambda = 3497{\cdot}540$ to $\lambda = 3441{\cdot}999$.

Six of the nine lines of this multiplet were examined in the magnetic field and it was found that it is due to the combination (pd) in the quintet system, the general formula being

$$n^5_{2i} - n^5_{3i}$$
$$i = 1, 2, 3, \quad i = 0, 1, 2, 3, 4.$$

The interval ratios are

$$\Delta p, \quad 72{\cdot}53 : 114{\cdot}07 = \begin{cases} 1{\cdot}9 : 3 \text{ obs.} \\ 2{\cdot}0 : 3 \text{ calc.} \end{cases}$$

this being the same as in the first triplet above,

$$\Delta d, \quad 58{\cdot}63 : 120{\cdot}00 : 187{\cdot}35 : 269{\cdot}28 = \begin{cases} 0{\cdot}9 : 1{\cdot}8 : 2{\cdot}8 : 4 \text{ obs.} \\ 1{\cdot}0 : 2{\cdot}0 : 3{\cdot}0 : 4 \text{ calc.} \end{cases}$$

Multiplet at $\lambda = 2427{\cdot}43$ to $\lambda = 2453{\cdot}65$.

This multiplet is related to the second triplet in the same way as the first multiplet is to the first triplet, and consequently it may be concluded that it also belongs to the septet system, that is to say, the general formula is

$$n^7_{2i} - n^7_{3i}$$
$$i = 2, 3, 4, \quad i = 1, 2, 3, 4, 5.$$

Owing to the distribution of the nine lines in three very narrow triplets, a quantitative determination of the Zeeman effect was impossible, but the above conclusion is confirmed by the interval ratios

$$\Delta p, \quad 176{\cdot}8 : 263{\cdot}6 = \begin{cases} 2{\cdot}7 : 4 \text{ obs.} \\ 3{\cdot}0 : 4 \text{ calc.} \end{cases}$$

similar to that of the second triplet,

$$\Delta d, \quad 3{\cdot}4 : 5{\cdot}4 : 8{\cdot}95 : 10{\cdot}6 \qquad \begin{cases} 1{\cdot}7 : 2{\cdot}7 : 4{\cdot}25 : 5{\cdot}3 \text{ obs.} \\ 2{\cdot}0 : 3{\cdot}0 : 4{\cdot}00 : 5{\cdot}0 \text{ calc.} \end{cases}$$

Although perhaps the evidence afforded by the last multiplet, owing to the small separations, is not very strong, it is eminently satisfactory that the Mn^1 spectrum is clearly based on odd terms, thus proving the

validity of the Kossel and Sommerfeld law of spectroscopic displacement.

The Relative Intensities of the Compound Lines of Multiplets.—The next matter which claims our attention is the relative intensities of the spectrum lines in multiple groups and the measurement of those has been achieved by Professor Ornstein and his colleagues in the University of Utrecht. This work forms a most valuable contribution to our knowledge of spectral series and is of very great importance. Professor Ornstein has been kind enough to write a complete account of the method employed and to add to this a theoretical discussion of the results obtained. He has done this with the particular object of its inclusion in the present chapter, and it is with a deep sense of my gratitude to him and with a full recognition of the honour he has conferred upon me that I give the following transcription of his monograph.

The measurement of the relative intensities of multiplet spectrum lines has been accomplished with the aid of photographic photometry. It is only in a few cases that direct measurements can be made by means of the thermopile and therefore a description of the photographic method of the measurement of intensity may be given.

The density of the photographic plate is a function of the time of exposure, the intensity of the light, the wave-length, and the conditions of development. The general form of this function is not known, and the special forms given by Schwarzschild, Stark, and Busé contain constants which vary from case to case. Now the only quantity which is important for our present problem is the intensity which produces a certain density, and in order that density may be used as a measure of relative intensity it is necessary that it be measured on the same plate under identical conditions of exposure and development. Instead of using an analytical expression for the relation between intensity and density, a graphic method of representation may be employed.

On the photographic negatives which are used for intensity measurements a scale of intensity must be printed, since the density itself gives no true measure of the intensity and is, indeed, an unknown function of it.[1] Before the detailed methods of observation are discussed, mention must be made of another fact which is of fundamental importance in these measurements of intensity. The density obtained on a photographic plate depends on the quantity of light energy which falls on it, but the same quantity of energy at different wave-lengths can give wholly differing densities, that is to say, the sensitivity of a photographic plate is different for light of different wave-lengths. In general, the sensitivity is not very different for two spectrum lines which do not differ in wave-length by more than 50-100 A. If, however, the distance between the component lines of a multiplet is greater than this, the wave-length sensitivity curve of the plate

[1] This very elementary fact has frequently been ignored.

must be determined, and methods suitable for doing this will be described.

As was stated above, in order graphically to compare the relative intensities of spectrum lines of nearly the same wave-length, we must print a density scale of this wave-length on the photographic plate. The most elegant way of doing this is to photograph the lines on the same plate with different intensities, the relation between these intensities being known. The advantage of this method is that it eliminates the effect of any fluctuations in the intensity of the source, so far as these do not influence the actual relative intensities of the lines themselves. There are many methods of obtaining the density marks which fulfil these conditions. Thus, with a prism spectrograph or an astigmatic grating we can proceed in the following way. A convex lens is homogeneously illuminated by the rays from the light source which is placed at its focus, and behind this lens are placed screens for decreasing the intensity of the light beam. By means of a second lens a sharp image of the screen is formed on the slit of the spectrograph. In this way each spectrum line is divided into sections with different intensities which give different densities on the photographic plate, and from these the characteristic curve expressing the intensity-density relation for that plate can be constructed. The screens are built up of rectangular portions of different transmissive powers which are accurately known. In the Utrecht Institute strips of neutral tinted glass have been used, but this glass has a disadvantage in that the transmissive power varies with the wave-length and is large in the red and violet regions of the spectrum. For this reason Professor Ornstein and Dr. Burger have more recently adopted the photographic screens used by Dr. Rassa Riwlin in her research on the absorptive power of liquid crystals.[1] It is an easy matter to make screens with an arbitrary number of steps and an arbitrary and adequate relation between the transmissive powers of the steps.

In order to prepare such an echelon screen, a lantern slide plate is illuminated with light of constant intensity for different times, different portions of the plate being of course employed, and then developed for a very long time. The transmissive power of the various regions is thereby determined as a function of the time of exposure at different wave-lengths with the aid of a monochromator, a thermopile, and a galvanometer. From these measurements a graph is obtained which expresses the transmissive power of the negative as a function of the time of exposure at each wave-length. A plate with the same emulsion, preferably from the same box, is then illuminated for times which will give the transmissive power desired, these times being read off from the time-transmissive power curve. The different parts of the plate are exposed successively, the rest of the plate being

[1] *Das Wesen der Lichtzerstreuung in flüssigen Kristallen*, van Druten, Utrecht, 1923.

screened by means of brass strips. In order to obtain homogeneity, the light source must be weak and placed at some distance away, and it is only possible in this way to obtain exposure times of sufficient length for exact measurement.

By this method of preparation echelon screens can be obtained which only show a very slight variation in transmissive power with the same wave-length. They can be used from the extreme red to $\lambda = 3600$ A., the variation in the transmissive power over this region being only a few parts per cent. The only disadvantage is that these photographed screens scatter the light to a certain extent, with the result that the transmission coefficient may depend on the optical arrangements. It is possible, however, to control the transmission by the method of varying the slit width, to be described presently.

Another type of echelon screen may be made by the deposition on quartz of metallic films, especially of platinum, by cathodic evaporation. Such screens can be used for the ultra-violet region, and they show more or less the same properties as do those prepared by the photographic method.

Yet another method has been described by Hansen.[1] An opaque screen with an opening cut in it of the shape shown in Fig. 19 is homogeneously illuminated by the rays from the source. By means of a cylindrical lens of short focal length and an ordinary lens an image of the aperture is made which consists of four parts, the intensities of which are proportional to the lengths of the four sections of the aperture.

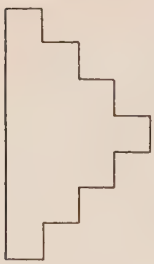

FIG. 19.

Frerichs[2] has described a method which was specially devised for use with the stigmatic grating mounting at the Bonn Institute. This fine type of mounting gives much more intense spectra than the astigmatic mountings, to which the two methods described above are restricted.

All the methods given have the advantage of giving the density marks at the same time as the spectrum lines. The disadvantage lies in the fact that the available intensity is not used very economically, with the result that long exposures are often necessary. Further, it is necessary to measure the transmissive power of the screens and this is somewhat laborious. It is possible to determine this quantity with a thermopile or photo-electric cell, and it is advisable to carry out the measurement with the help of the same optical system as that in which the screens are used in order to include the scattering effect already referred to. The method used for this purpose can also be used to print the density marks on the plate. In the method worked out by Ornstein and Burger, the density marks are imprinted on the plate with the same spectrograph as the spectrum lines, but with the continuous spectrum given by an incandescent lamp operated

[1] *Zeitsch. für Phys.*, **29**, 356 (1924). [2] *Ibid.*, **31**, 305 (1925).

on constant voltage. For the ultra-violet region a lamp with a quartz window is used and the lamp is run with an enforced intensity.

In actual practice the line spectrum is photographed on the plate, and for the density marks the continuous spectrum is photographed with different slit widths but with equal times of exposure in all cases. As the intensity of any part of a continuous spectrum is proportional to the slit width, provided that it is neither too small (when diffraction effects supervene) nor too large (when spectral impurity becomes too great), we obtain suitable density marks in this way. The time of exposure chosen for the whole sequence of line spectrum and density marks may be varied, but the density of the lines of the former must lie between the largest and smallest values of the density marks. Special measurements have shown that the intermittency of the source giving the spectrum lines under investigation has but little influence on the accuracy of measurement. The density marks may be obtained with relatively short exposures, twenty to thirty seconds, for each continuous spectrum. It is advisable to alternate the line spectrum and continuous spectrum on the plate so as to eliminate systematic errors in the sensitivity of the plate. Since most spectrographs give much diffuse light, narrow spectra should be taken by the use of a slotted screen in front of the plate.

Before we proceed to discuss the method of measuring the density and the graphical methods for determining the intensities, some words may be said about the sensitivity of the photographic plate as a function of the wave-length. It is well known that the plate is more sensitive to the violet than to the red. When specially sensitised to the red, there occur one or two minima of sensitivity in the green, and it is therefore absolutely necessary for us to know accurately the sensitivity as a function of the wave-length when measuring the relative intensities of lines which differ in wave-lengths by more than about 100 A. These difficulties can be overcome by using a continuous source, the spectral radiation of which is accurately known. It is possible to use black body radiation, but it is necessary that the radiation be really black. In Utrecht a common incandescent lamp has been used, which is under-run on constant voltage for the sake of lengthening its life.

We may briefly describe the method of standardising this lamp. A monochromator has been used which was built up of two identical spectroscopes in such a way that the spectrum formed by the first was folded together again by the second on to its own slit. Now, if we put a slit in the spectrum formed by the first spectroscope, that wave-length only which falls on this slit will pass through the complete instrument. The monochromator constructed by Dr. van Cittert in the Utrecht Institute excels in the intensity and spectral purity. In order to standardise a lamp with this monochromator we proceed as follows :—

In front of the monochromator is placed a strongly over-run lamp and by means of lenses an image of the lamp is formed on the

first slit. For the different colours corresponding to the different positions of the intermediate slit in the monochromator the intensity of this image is measured by means of a thermopile. Thereupon the intermediate slit is removed, a white image now being formed of which we know the spectral composition. By means of a lens an image of the latter image is formed in the slit of the spectrograph. Then at the point where the image of the over-run lamp had been formed, the lamp to be standardised is placed and a photograph is again taken. The stronger of the two images on the slit is weakened in the way described above in order to obtain the density marks for the comparison of the spectra of the two lamps. This comparison can be made at each wave-length, and, since the proportions of the energy in the image of the over-run lamp are known, those of the unknown lamp can be obtained.

For the ultra-violet a lamp with a quartz window may be used, but it is scarcely possible to measure the intensities by means of the thermopile since they are so small. In place of this a quartz mercury lamp, operated at a constant voltage, may be used, and this gives a very constant light source which contains rays of sufficient intensity for them to be directly measured with the thermopile. This method has been employed with a quartz monochromator.

The density of the photographs can be measured with a microphotometer. The two best types of this instrument are the thermo-electric microphotometer constructed by Moll [1] and the photo-electric instrument devised by Koch.[2] Both instruments give a measure of the quantity of the light which passes through the negative by the deflection of a galvanometer (Moll) or electrometer (Koch). The relative transmissive powers of the dark and transparent portions of the negative are given by the deflections of the galvanometer obtained when a constant beam of light after passage through the negative falls on the thermopile. As a quantitative measure of the density of a spectrum line we can take the deflection obtained with the dark image divided by the deflection obtained through the transparent part of the plate, and the negative logarithm to the base 10 of this relative transmissive power is generally known as the density. Now in order to compare the intensities of two spectrum lines, the characteristic curve for the plate must have been drawn, in which the logarithms of the intensities are plotted on the abscissæ and the densities or relative transmissive powers are plotted on the ordinates. The maximum intensity is put arbitrarily at 100.

In Fig. 20 are shown two characteristic curves for two wave-lengths λ and λ', such as are obtained when the densities have been measured in the manner described. In order to find the ratio of the intensities we can proceed by graphical interpolation, remembering that the maximum intensity is always 100, or 2 on the logarithmic

[1] *Proc. Phys. Soc.*, London, **33**, 207 (1920-21).
[2] *Ann. der Phys.*, **39**, 705 (1912); *Zeitsch. für Instrumentenk.*, **41**, 313 (1921).

scale. If $(\lambda' - \lambda)/\lambda \ll 1$, then the sensitivity of the plate will be the same for the two wave-lengths and the ratio may be found by measuring the distance A′A on the logarithmic scale of intensity. A much more accurate way is to take advantage of the fact that the two curves are parallel to one another, and that the difference between the logarithms of the intensities for two equal densities gives the ratio of the intensities. It follows that the mean distance measured from the maximum value 2 on the logarithmic scale gives the ratio of the

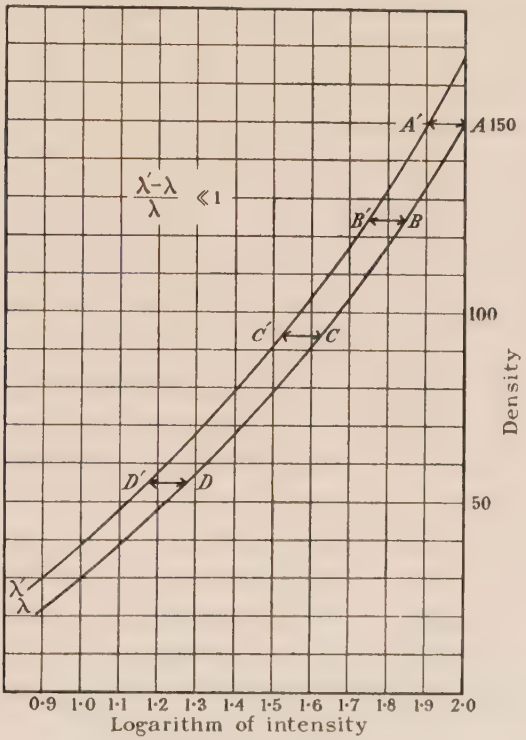

FIG. 20.

intensities. The errors of the plate are eliminated to a large extent in this way.

The same method can also be used for the curves when the relative transmissive power is plotted against the logarithm of the intensity, since the curves are also parallel to one another when the distance in wave-length is not too great. In both methods with six density marks the measurements give results which are accurate to within 3 per cent.

There is one point to be borne in mind when density marks are

being imprinted on a plate. Most spectra show a continuous background owing partly to unresolved band spectra, and partly to stray light due to reflections within the instrument, or to dust on the lenses and prisms, or to inequalities in their surface, etc. The presence of stray light of different wave-length from that measured must be avoided as much as possible, since it may give rise to entirely incorrect results. With line spectra the error with large dispersion is less than it is with small; if necessary a colour screen may be used to cut out the most dangerous wave-lengths, namely, those to which the photographic plate is more sensitive, such for example as the blue or violet when measurements are being made in the red. The continuous background caused by light of the same or very nearly the same wave-length can be eliminated by measuring the density in the neighbourhood of the line under consideration. The non-blackened part must be measured at some distance from the line. From the characteristic curves the intensity of the background can be determined, and the ratio of the intensities of the lines is measured after this background intensity has been subtracted.

As an example of the method of procedure, the measurements of the intensities of the lines in one of the iron multiplets is given below. If the density marks are obtained by the method of variation of the slit width, the characteristic curves must have been constructed with the help of continuous spectra. From these curves the ratio of intensities of the lines can be obtained by reading the corresponding intensities on the density curves given by the lines. The method gains some control if the lines are photographed several times on the plate with different densities. This is possible without special difficulty if the line source does not illuminate the slit homogeneously, or still more certain if the illumination is homogeneous and the slit is divided into two or more parts by an echelon screen. In this latter case, however, it is not necessary to know the coefficients of transmission of the sections of the screen.

It must be noted that in all the methods in which echelon screens are used it is necessary that the slit be homogeneously illuminated, this not being so in the slit width variation method. In the former, therefore, it is always advisable to have 100 per cent. transmission on both sides of the echelon and, if possible, to repeat one of the other scales.

If the ratio of the intensity is to be determined of spectrum lines for which the sensitivity of the plate is different, we must proceed in a slightly different way. We photograph the line spectrum on the plate, using the echelon screens, and on the same plate we also photograph the spectrum of the standardised lamp with the help of the echelon screens. The time of exposure for the two must be so chosen that the densities obtained with each will be in the same region. Let λ_1 and λ represent the characteristic curves for the line spectrum, and λ_1' and λ' those for the spectrum of the standardised lamp. The distances on the logarithmic intensity scale $\lambda - \lambda'$ and $\lambda_1 - \lambda_1'$ give the

PLATE I.

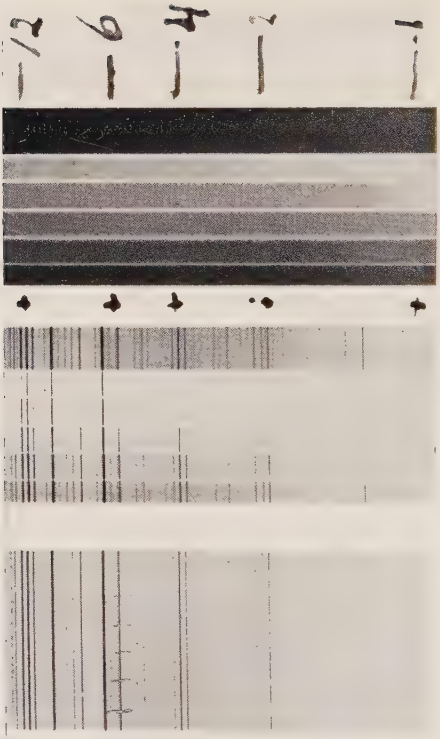

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PLATE II.

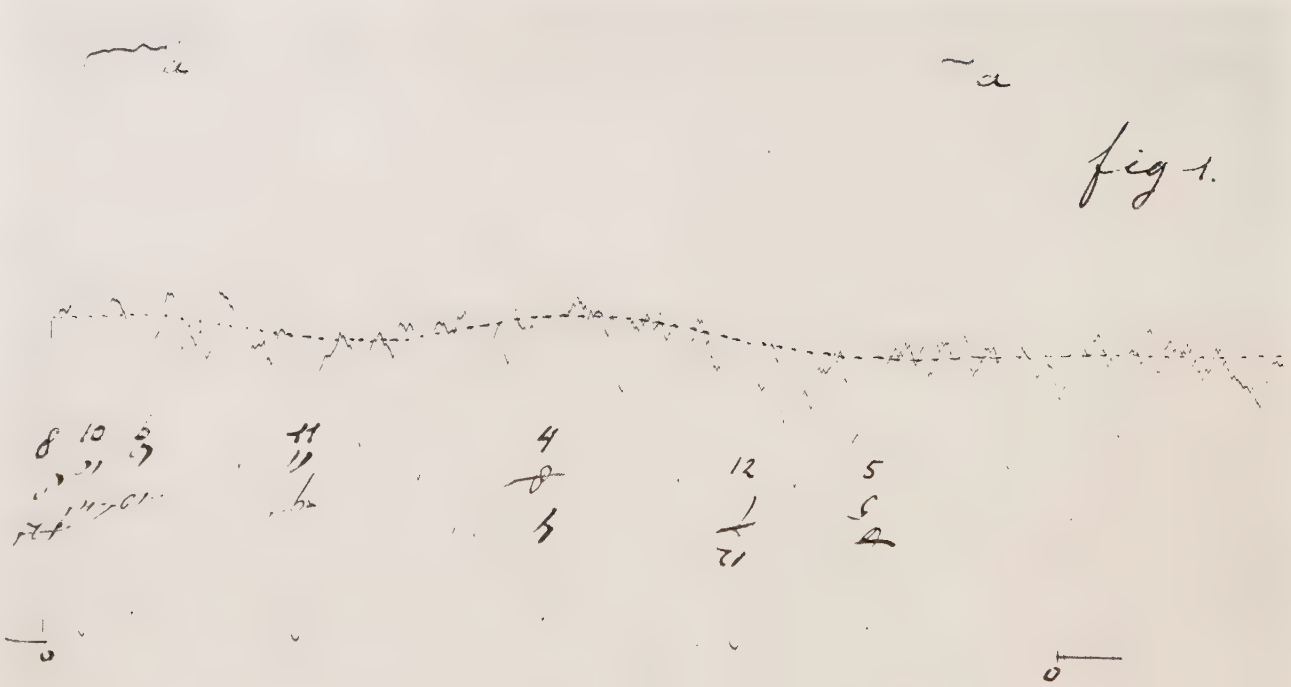

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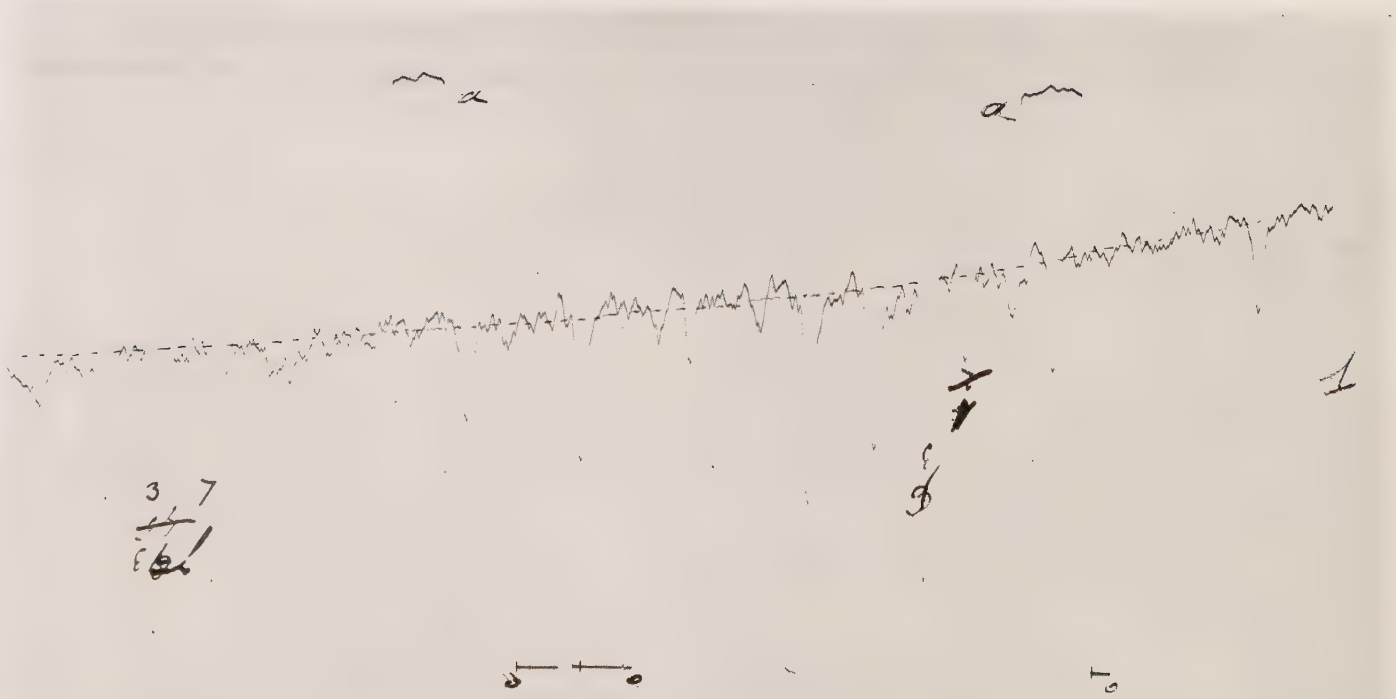
PLATE III.



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ratio of intensities in the line spectrum to those in the lamp spectrum at the same wave-length. In the lamp spectrum the ratio of the intensities of the wave-lengths λ and λ_1 is known, and consequently the ratio of the lines may be obtained from the curves.

The methods described in the foregoing can also be applied to the Röntgen region, as has been shown by Bouwers in his Utrecht dissertation. Since these methods have their origin in the measurements of absorption carried out by Dr. Rassa Riwlin, it may be argued that they can be applied to absorption bands without difficulty when these are broad. The photographic measurement of narrow absorption lines is very difficult. Not only is the effect due to the filtering of the absorbed light in the band very large and indeterminate, but the photographic plate for narrow limits does not give a density which corresponds to the intensity of the radiation falling on it, it not being possible to determine accurately the function governing the relation.

It is necessary also to mention another difficulty which arises when intensity measurements are carried out with the help of instruments such as the echelon grating, the étalon, and the Lummer-Gehrcke plate. The intensity distribution found by the foregoing method with photographed spectra is not a true picture of the intensity distribution in the light which falls on the slit of one of these instruments. For each of these instruments the intensity distribution must be calculated in the proper way from the intensities in the interference image. This has been done for the echelon grating by van Cittert and van Geel in the Utrecht Institute, and for the Lummer-Gehrcke plate by Hansen in Jena.

We may now describe in detail the measurement of the intensities of the lines in one of the multiplets of the iron spectrum. In Plate I. is shown a reproduction of the spectra taken with the astigmatic grating of the Utrecht Institute. Reading from the bottom upwards there are shown :—

1. The iron spectrum between $\lambda = 5712{\cdot}1$ and $\lambda = 5569{\cdot}6$ photographed without echelon screens.

2. The same photographed with echelon screens.

3. The spectrum of a standardised lamp photographed with echelon screens. The two sets of density marks were taken with a photographed echelon screen mounted on the homogeneously illuminated lens. The first iron spectrum was taken in order to eliminate errors which may have been introduced by non-homogeneous illumination of the slit. Photograms were taken with the Moll microphotometer of each of the spectra shown in Plate I., and in Plates II. and III. is reproduced the registered curve showing the galvanometer deflections given by one of the iron spectra. The straight line (0) at the bottom of the figure is the zero line of the instrument, and the short lines (*a*) at the top give the deviation of the galvanometer at transparent regions of the plate. The sharp peaks of the registered curve are due to the spectrum lines. The dotted curve joins those points which give a measure of the deviation of the galvanometer in the continuous

background of the spectrum. The lines of the multiplet are indicated by arabic numbers.

In Plate IV. is shown one of the registered curves for the spectrum

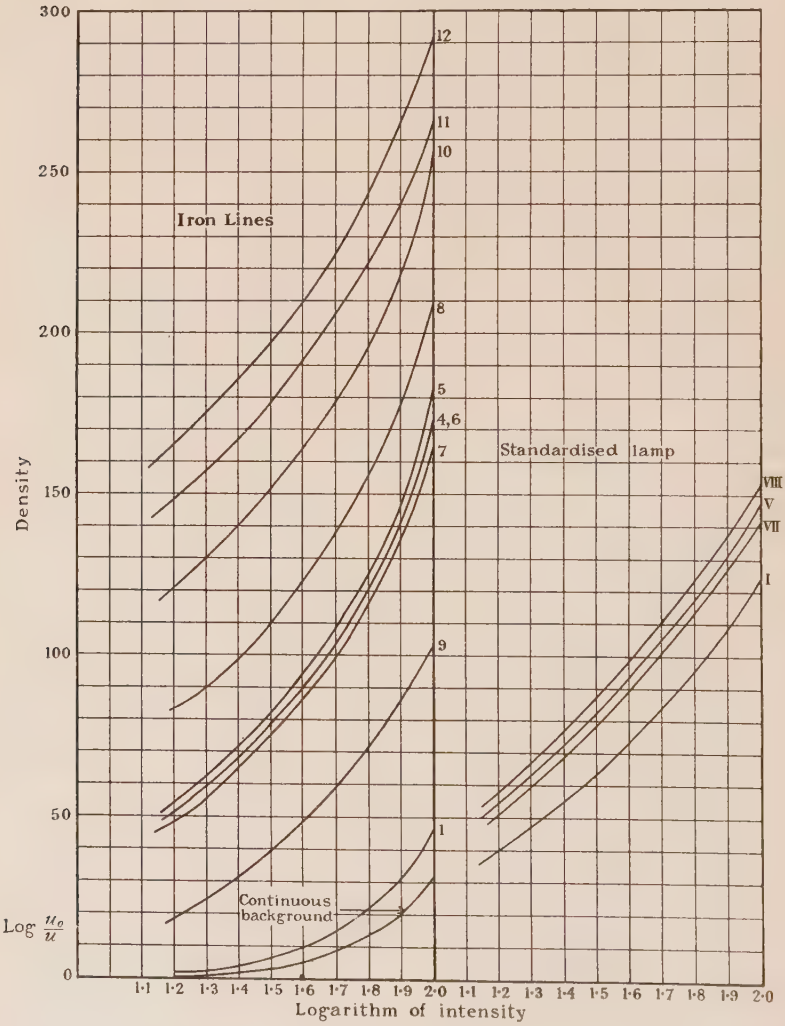

FIG. 21.

of the standardised lamp, namely, that for the wave-length $\lambda = 5688{\cdot}8$, and this spectrum has been registered in a direction perpendicular to its length, the peaks in the curve being given by the gaps between the six spectra shown in Plate I.

PLATE IV.

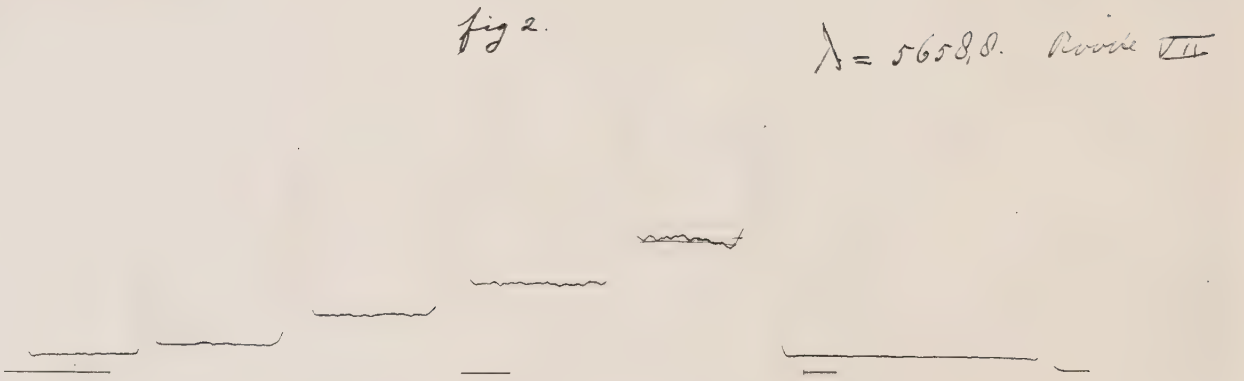

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PLATE V.

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In Fig. 21 are given the characteristic curves for the spectrum lines and for the standardised lamp. In the latter those marked VIII., V., VII., and I. correspond to the wave-lengths 5569·6, 5624·5, 5658·8, and 5712·1. From these latter curves we find that, if we put the intensity of the region VIII. equal to 100 on an arbitrary scale, V., VII., and I. show the intensities 92, 85, and 67·5. This can be arrived at from the mean distance of the characteristic curves in the manner already shown. Now, in the spectrum of the standardised lamp the ratio of the intensities in the regions under consideration is given by 7·3 : 8·35 : 8·9 : 9·8, which leads to reduction factors for the intensity scales of those lines given by

$$\frac{100}{7\cdot3} : \frac{92}{8\cdot35} : \frac{85}{8\cdot9} : \frac{67\cdot5}{9\cdot8} = 100 : 80\cdot5 : 69\cdot7 : 50\cdot5.$$

By graphical interpolation, which can be done by means of a straight line, the reduction factor for every intermediate wave-length can be determined.

In Table LXV. are set forth the final results.

TABLE LXV.

No. of line.	I_1.	r.	I_0.
1	1	50·5	1·98
4	27·5	86·5	31·8
5	32	80·5	39·7
6	27·5	96·2	28·7
7	26	69·7	37·6
8	55	100	55
9	10	50·5	19·9
10	95	98·5	97
11	130·8	92	143
12	187	85	225

I_1 is the intensity of the line on the arbitrary scale, r is the reduction factor, and I_0 is the true intensity after reduction by means of the standardised lamp curves.

The corrections to be applied for the continuous background were 4 for line 1 and 5 for the other lines.

In Plate V. is given a reproduction of the photographed register of the galvanometer deflections obtained in the density measurements of the p-components of the Zeeman pattern of the magnesium line at $\lambda = 5183$. In this case the lines are very close together so that the characteristic curves expressing the intensity-density relation are parallel and in consequence the density marks have been obtained by the use of an echelon screen with steps which have transmissive powers of 90, 65, 24, 9·6, 57, and 100 per cent., respectively. I have introduced this Utrecht record here because it shows well how Professor

Ornstein's method is applied to the measurement of the intensity ratios of the components of Zeeman patterns.

Professor Ornstein has appended to the foregoing an account of the theoretical aspect of the subject, which may now be given.

The intensity of a spectrum line depends on two factors,

1. The concentration of the initial level.
2. The probability of the transition.

Now the first quantity depends very largely on the circumstances. It is possible, for example, to excite sodium vapour in such a way that the lower p-level only is called into play, and in this case one only of the D-lines appears as an emission line if the density of the vapour is sufficiently low. In other cases, however, the excitation is such that both levels are excited. The more irregular is the excitation, the greater is the probability that levels of nearly the same energy are excited to an amount which is proportional to the *a priori* probability of the levels.

The probability of the transition is influenced to a much smaller extent by external circumstances, and it can be regarded as a true atomic quality. Bohr and Kramers have estimated the intensities of the hydrogen lines in the Stark effect. The newer developments of the quantum theory accentuate the view that the ensemble of the probabilities of transition (the Fourier components) is the only reality of the atom.

Now in experimental work on intensity ratios it is in general difficult to determine the concentration of the atoms at different levels, and in consequence it was necessary to undertake the measurements of the ratio of the intensities of the lines which are given by transitions from a single initial level to two or more final levels. Such lines are given by the $2\pi - m\sigma$ series of the alkali metals. From the single σ-level transitions occur to the two π-levels, with of course the emission of a doublet. The ratio of the intensities of these lines depends only on the probability of the transitions $m\sigma \rightarrow 2\pi_1$ and $m\sigma \rightarrow 2\pi_0$. It is possible that the intensity of the observed line depends on the transition by absorption (self-reversal), since the concentration of the $2\pi_1$ and $2\pi_0$ levels can be different. Experiment, however, has shown that this is not the case with arc and flame spectra, if the concentration of the salt is not too great.

The measurements carried out by Dorgelo in the Utrecht Institute have established the intensity ratio of 2 : 1, with a probable error of 3 per cent., in the following doublets : sodium, $2\pi - 2\sigma$ and $2\pi - 3\sigma$. For the triplet systems, $2p - 2s$, of magnesium, calcium, zinc, and cadmium, the ratio of intensities was 5 : 3 : 1, within the same degree of accuracy.

A remark made by Sommerfeld at the Physikertag at Bonn in 1923 led to a generalisation of these results, which could be verified by experiment. Sommerfeld drew attention to the fact that the transition probabilities could be expressed by the inner quantum

numbers of the final levels. The inner quantum numbers for the p-levels in doublet, triplet, quartet, etc., systems are

$$i = \tfrac{3}{2}, \tfrac{1}{2}\ ;\ 2, 1, 0\ ;\ \tfrac{5}{2}, \tfrac{3}{2}, \tfrac{1}{2}\ ;\ 3, 2, 1\ ;\ \text{etc.}$$

The statistical weight of the levels is related to their inner quantum numbers and is given by the number of possible orientations in a magnetic field, this being $2i + 1$. The statistical weights therefore are

Doublet.	Triplet.	Quartet.	Quintet.	Sextet.	Septet.	Octet.
4, 2	5, 3, 1	6, 4, 2	7, 5, 3	8, 6, 4	9, 7, 5	10, 8, 6

Now the intensities for the sp members of the doublet and triplet systems are given exactly by the statistical weights of the p-levels, and it became of great interest to investigate whether this rule is generally true. For the triplet in the sextet and octet systems of manganese ($\lambda = 6021$, 6016 and 6013, and $\lambda = 4823$, 4785, and 4754) the intensity ratio was found to be 100 : 77 : 53 or 4 : 3 : 2, and 100 : 80 : 61 or 5 : 4 : 3, respectively. The rule therefore was fully confirmed.

The measurements of the intensity ratios in the diffuse series of the alkali metals have led to very interesting results. In the case of sodium, potassium, and rubidium, the d-levels are so close together that the members of this series appear as doublets, and the intensity ratio in each case was found to be 2 : 1. In the case of cæsium the d-levels are sufficiently far apart for the lines due to them to be seen separated, with the result that the ratio of the intensities of the three lines of the complex doublet can be measured. The statistical weights of the d-levels are 6, 4, those of the p-levels 4, 2, as before, and the possible transitions can be written $6 \to 4$, $4 \to 4$, and $4 \to 2$. The experimental observations have shown that the sum of the intensities of the two transitions $6 \to 4$ and $4 \to 4$ is double that of the transition $4 \to 2$, and that the ratio of the sum of the intensities of the transitions $4 \to 4$ and $4 \to 2$ to that of the transition $6 \to 4$ is 6 : 4. This result suggested to Dr. Burger the so-called summation rule, which can be formulated as follows :—

In a multiplet the ratio of the sum of the intensities of the lines due to transitions starting from the same level to the sum of the intensities of the lines due to transitions starting from another level is given by the statistical weights of those levels, and, conversely, the sum of the intensities of the lines due to transitions to the same level is proportional to the statistical weight of this level.

The truth of this rule has been confirmed not only in the Utrecht Institute, but also by the later work of Dorgelo at the laboratories of the Philips lamp works and also in the Physical Laboratories at Bonn.

It is very remarkable that these simple relations, based on the inner quantum numbers, should hold and that the conditions of excitation should in general exert no influence. It must, however, be

borne in mind that the latter may play an important rôle either by self-reversal or by specific excitation of some of the levels. It is interesting that the summation rule can be stated in another form which bears a relation to the radiation law. If we take, for example, the sp_1 and sp_0 doublets, then the intensities of these lines will be proportional to the numbers of the atoms, N_1 and N_0, which exist in the p_1 and p_0 levels, and to the Einstein emission coefficients, A_{sp_1} and A_{sp_0}, of those levels. We have therefore

$$N_1 A_{p_1 s} : N_2 A_{p_0 s} = 4 : 2.$$

If we suppose that the number of atoms in which the electron is in the p_1 and p_0 levels, respectively, is proportional to the statistical weight of the levels, g_1 and g_0, and to the factors $exp - \frac{\epsilon_1}{KT}$ and $exp - \frac{\epsilon_0}{KT}$ as indicated by the Boltzmann principle, we have

$$\frac{g_1 A_{p_1 s}\, exp - \frac{\epsilon_1}{KT}}{4} = \frac{g_0 A_{p_0 s}\, exp - \frac{\epsilon_0}{KT}}{2}.$$

If the difference $\epsilon_1 - \epsilon_0$ is small compared with KT, which is true for most levels in the case of flame and arc spectra, we have

$$\frac{g_1}{4} A_{p_1 s} = \frac{g_0}{2} A_{p_0 s}$$

and since we know that

$$\frac{g_1}{4} = \frac{g_0}{2}$$

it follows that $A_{p_1 s} = A_{p_0 s}$.

The probability of emission, therefore, for two p-levels is the same when the transition to the same s-level takes place.

It is easy to generalise the Burger summation rule to the theorem : If lines are emitted by transmissions from multiplet levels, the sum of the probabilities for the lines from each level is the same for those levels. An equivalent theorem can be formulated for the lines which originate in transitions ending on the same level. If we consider the sp_1 and sp_0 lines, the relative intensities will be proportional to the probabilities of transition, $A_{p_1 s}$ and $A_{p_0 s}$, as the final level is the same for both lines. The experimental result is now

$$\frac{A_{p_1 s}}{4} = \frac{A_{p_0 s}}{2}.$$

Now Einstein has shown in his theory of radiation that there must exist a simple relation between the coefficient of emission and the coefficient of absorption (B_{sp}) per unit energy for the same line. If g_s represents the statistical weight of the s-level, the Einstein relation is

$$g_s A_{p_1 s} = \frac{8\pi}{c^3} h \nu_{sp_1}^3 g_{p_1} B_{sp_1},$$

where ν_{sp_1} is the frequency of radiation and h is the Planck constant. If we put

$$g_{p_1} : g_{p_0} = 4 : 2,$$

then

$$\nu^3_{sp_1} B_{sp_1} = \nu^3_{sp_0} B_{sp_0}.$$

This result can be generalised to more complex cases. If the difference between the p_1 and p_0 levels is small, the relation takes the form

$$B_{sp_1} = B_{sp_0},$$

that is to say, the absorption coefficient for levels with a small difference in energy is the same for lines which bring the atom to the same level. It is very interesting to note that the formula takes a very simple form if the absorption coefficient per quantum is introduced, and if the probability of absorption is resolved into two factors, the one factor expressing the probability of the collision of a light quantum with an atom, this being proportional to λ^2, and the other factor expressing the probability of absorption if a collision takes place. So far as the latter factor is concerned, the rule in general is valid in the form which it takes for the case of levels differing only slightly in energy.

In the further development of the theory of intensities as the result of the work of Ornstein and Burger, Sommerfeld and Höhnl, Goudsmit and Kronig, Russell, Kemble, Duke, and others, the Bohr correspondence principle has played a considerable part. As the result of Sommerfeld and Heisenberg's paper, in which they were able to derive a formula for intensity from the study of a simple model, it has been found possible to enunciate a general formula for the intensities of the lines of multiplets and of Zeeman patterns, and also in cases where the Burger summation rule is unable to determine the individual intensities. The rule is true for all such cases, but the number of unknown intensities is greater than the number of equations given by the application of the rule. The formula for the intensity of Zeeman patterns as given by weak fields has been verified by experiments so far as observations have as yet been made. The generalisations mentioned above, however, do not give the relative intensities of some of the faint components of multiplets, as very careful experiments carried out at Utrecht have proved. The same rules are derived by the new quantum treatment of Heisenberg, Born, and Jordan.

It may be mentioned that attempts have been made to apply the summation rule to band spectra, both from the theoretical standpoint by Kemble, Höhnl, and London and Diecke, and on the experimental side by Frerichs and others at Bonn. These have shown that the generalisation of the rule is possible and that heat motion has an influence on intensity which can be defined by the Boltzmann principle. Lastly, some investigations have shown that the rule can be applied to the K and L doublets of the Röntgen spectra.

The following is a list of the papers dealing with this subject which have been published :—

" Die Intensität der Mehrfachlinien und ihre Zeemancomponenten," A. Sommerfeld and W. Heisenberg, *Zeitsch. für Phys.*, **11,** 131 (1922).

" Un monochromateur de grande luminosité et avec peu de lumière diffuse," P. H. van Cittert, *Rev. d'Opt.*, **2,** 57 (1923).

" Contribution à la theorie du spectroscope à échelon. Verification experimentale," W. C. van Geel, *Rev. d'Opt.*, **2,** 445 (1923).

" Über die Schwärzung der photographischen Platte durch Röntgenstrahlen und ihre Anwendung an Intensitätsmessung," A. Bouwers, *Zeitsch. für Phys.*, **14,** 374 (1923). Also *Dissertation*, Utrecht, 1924.

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A few words may be added to the foregoing with respect to the Burger and Dorgelo summation rule. In their original paper they gave four rules and these may be quoted here.

The first rule states that the intensity ratios of the lines of doublets and triplets of the sharp series are equal to the intensity ratios of the inner quantum numbers (I) of the final levels. In this rule we find

the quantitative expression of the qualitative law of Sommerfeld which was given previously on p. 114.

This rule also holds good if the initial level is complex and the various terms are so little different that they cannot be resolved. In the combination $\pi_i - \delta_i$ where the δ-terms are so close that they cannot be resolved, the intensities of the lines are proportional to the values of I for the final or π_i terms, *i.e.*, 2 : 1. Again, in the fundamental series of calcium where the fundamental term is not resolved, the intensities of the lines are in the ratio 7 : 5 : 3, which is the same as that of the Landé inner quantum numbers. In these cases some of the lines are complex and not resolved, and their intensities are therefore the sums of the intensities of the lines having the same final level. From this a second rule may be deduced: The sums of the intensities of the lines due to transitions which have the same final level are proportional to the inner quantum numbers of the final levels. This is shown to be true from the following table of intensities of the lines of the first diffuse triplet ($1p_i - 2d_i$) of calcium :—

	$1p_1 - 2d_3$	$1p_1 - 2d_2$	$1p_1 - 2d_1$	$1p_2 - 2d_3$	$1p_2 - 2d_2$	$1p_3 - 2d_3$
λ =	4456·61	4455·88	4454·77	4435·67	4434·95	4425·43
Intensity	1	18	100	19	54	25

The three final levels are $1p_1$, $1p_2$, and $1p_3$, and the sums of the intensities of the lines which arise from transitions to these levels are, respectively, 1 + 18 + 100 = 119, 19 + 54 = 73, and 25.

The ratio of these intensities is very nearly proportional to the inner quantum numbers of $1p_1$, $1p_2$, $1p_3$, thus

$$119 : 73 : 25 = 5 : 3 : 1.$$

The divergence from exact proportionality is readily explained by the fact that the measured intensities of the stronger lines are too small owing to their self-reversal.

As a corollary to rule I. Burger and Dorgelo find a third rule, namely, that the intensities of the lines of the principal series are proportional to the inner quantum numbers of the initial levels. As an instance of the validity of this we may quote the case of the principal triplet ($1s - 2p_i$) of mercury, the ratio of the intensities of the lines (5 : 3 : 1) being the same as the ratio of the inner quantum numbers of $2p_1$, $2p_2$ and $2p_3$.

As a corollary to rule II. we have a fourth rule to the effect that sums of the intensities of the lines arising from transitions having the same initial levels are proportional to the inner quantum numbers of those initial levels. This can be exemplified by the calcium triplet already given in the above table, the intensities being arranged according to the scheme shown in Table LXVI.

The inner quantum numbers (I) are given immediately after the symbols for the various levels. Rule II. states that the sums of the intensities in the horizontal rows are proportional to the values of I for the *d*-terms, that is to say (1 + 19 + 25) : (18 + 54) : 100 = 3 : 5 : 7.

TABLE LXVI.

$1p_1\left(\frac{5}{2}\right)$	1	18	100
$1p_2\left(\frac{3}{2}\right)$	19	54	0
$1p_3\left(\frac{1}{2}\right)$	25	0	0
	$2d_3\left(\frac{3}{2}\right)$	$2d_2\left(\frac{5}{2}\right)$	$2d_1\left(\frac{7}{2}\right)$

We still have to consider the intensities of the individual lines in a multiplet, and Burger and Dorgelo by application of their four rules given above succeeded in developing a method of expressing these. The sum of the intensities of all the lines is put equal to unity and the intensities of the lines are expressed as a fraction, the common denominator of which is the product $2RK \cdot 2R'K'$ where RK and R′K′ stand for the values of R and K for the initial and final levels respectively. The values of I/2RK are placed in a horizontal row of a table and the values of I/2R′K′ in a vertical column, and the possible combinations between the various terms are considered. Those which are forbidden by the selection principle are given the intensity 0 and those lines for which the transition in I differs most from the simultaneous transition in K are given the intensity $1/(2RK \cdot 2R'K')$, (Sommerfeld's law of minimum intensity). Then the sum of the intensities of all the components in each vertical column must equal the value of I/2RK for that column, and the sum of the intensities in each horizontal row must equal the value of I/2R′K′ for that row. As an instance of this we may take the case of the fundamental triplet (*df*) and the values calculated for the *d*- and *f*-terms are arranged in Table LXVII.

TABLE LXVII.

I/2RK	$\frac{5}{21}$	$\frac{7}{21}$	$\frac{9}{21}$	
3 / 15	$\frac{63}{315}$	0	0	n^3_{31}
5 / 15	$\frac{11}{315}$	$\frac{94}{315}$	0	n^3_{32}
7 / 15	$\frac{1}{315}$	$\frac{11}{315}$	$\frac{135}{315}$	n^3_{33}
	n^3_{42}	n^3_{43}	n^3_{44}	

The three combinations $n^3_{31} - n^4_{43}$, $n^3_{31} - n^3_{44}$, and $n^3_{32} - n^3_{44}$ are forbidden by the selection principle and therefore the values of 0 are assigned to these. The smallest intensity is given by the transition $n^3_{33} - n^3_{42}$, since the I transition is in the opposite sense to the K transition, and consequently the resulting line is given the intensity $1/(21 \times 15) = 1/315$. The remaining intensities are then found from the summation rule stated above. If these intensities are reduced so that the most intense line has the intensity 100 we obtain the following values :—

d_1	46·7(48)	0	0
d_2	8·1(9)	69·6(69)	0
d_3	0·7(1)	8·1(9)	100(100)
	f_1	f_2	f_3

The bracketed values are those observed in the strontium triplet $1d - 3f$.

The Multiplets of Chromium and Iron.—We may now return once more to the experimental side of the problem and it will be remembered that the case of chromium had only been dealt with by Catalan in a very preliminary fashion, he having found three multiplets, one of nine lines and two of twelve lines. In later papers he succeeded in identifying many more multiplets in this spectrum, and in allocating these to their respective series. He further showed that there are present five-fold and seven-fold terms.[1]

The chromium arc spectrum was also investigated by Fraülein Gieseler who published her first paper almost at the same time as Catalan's first paper appeared, and in her second paper she was able to extend some of the series to include higher members than Catalan was able to do.[2] Moreover, she confirmed her allocation of the lines by means of observations on the Zeeman effect.

The largest term entering into the chromium spectrum is a sharp term and has the value in wave-numbers 54640·9 (Catalan) and 54541·26 (Gieseler) and it is to be noted that Catalan expresses the wave-lengths in I.A. whilst Fraülein Gieseler uses the Rowland standard. The electron orbit is part of a septet system and is a $4s$-orbit and therefore on Landé's system the term is denoted by 4^7_{13}, the term being called $1s$ by Catalan. In this septet system there are the single s-term, two three-fold p-terms and a five-fold d-term, and the difference between the two p-terms in wave-numbers is 4436·4 (Catalan). No evidence has as yet been found of the fundamental series. There exist therefore two parallel systems of series belonging to the septet system, which are separated as regards the first lines of each member by 4436·4.

[1] *Compt. Rendus*, **176**, 84 (1923); *Anales Soc. Espan. Fis. y Quim.*, **21**, 84 (1923).

[2] Hilda Gieseler, *Ann. der Phys.*, **69**, 147 (1922); *Zeitsch. für Phys.*, **22**, 228 (1924).

In Table LXVIII. are given the two sharp and two diffuse series as arranged by Catalan, the symbols for the terms being those fixed by Fraülein Gieseler.

TABLE LXVIII.

First Sharp Series, $4^7_{2i} - n^7_{13}(4p_i - ns)$.

$i = 4, 3, 2.$

$4^7_{24} = 31142{\cdot}0, \quad 4^7_{23} = 31254{\cdot}5, \quad 4^7_{22} = 31335{\cdot}9.$

λ in I.A.	Int.	ν.	$\Delta\nu$.	n.	n^7_{1s}.
− 4254·33	10R	− 23498·9			
			112·6		
− 4274·80	9R	− 23386·3		4	54640·9
			81·4		
− 4289·72	9R	− 23305·0			
7462·34	10	13396·9			
			112·5		
7400·22	9	13509·4		5	17745·1
			81·4		
7355·93	9	13590·8			

Second Sharp Series, $4^{7a}_{2i} - n^7_{13}(4p^a_i - ns)$.

$i = 4, 3, 2.$

$4^{7a}_{24} = 26705{\cdot}6, \quad 4^{7a}_{23} = 26870{\cdot}7, \quad 4^{7a}_{22} = 26962{\cdot}6.$

λ in I.A.	Int.	ν.	$\Delta\nu$.	n.	n^7_{1s}.
− 3578·686	10R	− 27935·27			
			115·04		
− 3593·485	9R	− 27820·23		4	54640·9
			91·40		
− 3605·330	9R	− 27728·83			
1157·1	9	8960·4			
			115·2		
11015·5	8	9075·6		5	17745·2
			91·4		
10905·7	6	9167·0			

First Diffuse Series, $4^7_{2i} - n^7_{3i}(4p_i - nd_i)$.

$i = 4, 3, 2.$ $\quad i = 5, 4, 3, 2, 1.$

$4^7_{24} = 31142{\cdot}0, \quad 4^7_{23} = 31254{\cdot}5, \quad 4^7_{22} = 31335{\cdot}9.$

λ in I.A.	Int.	ν.	$\Delta\nu$.	n.	n^7_{3i}.
5329·80	2	18757·2			
			2·3		
5329·15	5	18759·5			$4^7_{35} = 12379{\cdot}6$
			2·9		
5328·34	10	18762·4			$4^7_{34} = 12382{\cdot}5$
			112·5		
5298·45	(Calc.)	18868·2			
			1·5	4	$4^7_{33} = 12384{\cdot}7$
5298·02	6	18869·7			
			2·3		
5297·39	8	18872·0			$4^7_{32} = 12386{\cdot}4$
			81·8		
5276·07	7	18948·3			
			1·1		
5275·76	7	18949·4			$4^7_{31} = 12387{\cdot}6$
			2·1		
5275·17	6	18951·5			
4130·62	(Calc.)	24203·5			
			2·9		
4130·13	(Calc.)	24206·4			
			4·5		$5^7_{35} = 6931{\cdot}1$
4129·36	5	24210·9			
			112·5		$5^7_{34} = 6935{\cdot}6$
4111·82	1	24314·2			
			1·8	5	
4111·51	3	24316·0			$5^7_{33} = 6938{\cdot}5$
			2·9		
4111·02	4	24318·9			
			81·4		$5^7_{32} = 6940{\cdot}3$
4099·80	3	24394·2			
			1·3		
4098·11	3	24395·5			
			1·9		$5^7_{31} = 6941{\cdot}7$
4097·39	2	24397·4			

TABLE LXVIII.—*Continued.*

SECOND DIFFUSE SERIES, $4^{7a}_{2i} - n^7_{3i}(4p^a_i - nd^7_i)$.

$i = 4, 3, 2.$ $i = 5, 4, 3, 2, 1.$

$4^{7a}_{24} = 26705{\cdot}6.$

λ in I.A.	Int.	ν.	Δν.	n.
6981·04	2	14321·0		
			2·1	
6980·81	7	14323·1		
			2·7	
6979·79	10	14325·8		
			115·0	
6925·99	2	14434·4		
			1·6	
6925·20	9	14436·0		4
			2·3	
6924·14	10	14438·2		
			91·5	
6883·03	9	14524·5		
			1·4	
6882·38	9	14525·9		
			1·6	
6881·62	9	14527·5		
5057·50	(Calc.)	19767·1		
			2·9	
5056·76	(Calc.)	19770·0		
			4·5	
5055·59	4	19774·5		
			115·5	
5028·71	(Calc.)	19880·3		
			1·8	
5028·25	2	19882·1		5
			2·8	
5027·54	3	19884·9		
			91·4	
5006·05	3	19970·4		
			1·0	
5005·77	3	19971·4		
			2·1	
5005·24	2	19973·5		

Fraülein Gieseler has added another complete term to the first sharp series and has identified the strongest component of the third member of the second sharp series. She has therefore obtained the three values of the sharp terms, $n = 4, 5, 6$, and in terms of Rowland's standard these are

$$4^7_{13} = 54541{\cdot}26$$
$$5^7_{13} = 17647{\cdot}18$$
$$6^7_{13} = 8899{\cdot}28.$$

These are expressed by the Ritz formula,

$$n^7_{13} = \frac{N_{cr}}{[n + s^7 + \sigma^7(ns^7)]^2}$$

where $N_{cr} = 109735{\cdot}95$, $s^7 = 0{\cdot}52965$, $\sigma^7 = -2{\cdot}0383 \times 10^{-6}$. The differences (obs. — calc.) for $n = 4$, 5, and 6 are + 2·76, — 0·69, and — 0·18, respectively.

The first terms of the two principal series have the same values as those of the two sharp series, but unfortunately no other terms have as yet been recognised.

The quintet system has been much more completely worked out than the septet system, and inasmuch as this indicates the complexity which exists in such cases I will give the whole scheme in detail. The system is in reality perfectly straightforward, but it is rendered more complicated by the fact that there are present four different three-fold terms which must be principal terms since they combine with

both *s*-terms and *d*-terms. This leads to the existence of parallel series which are analogous to those already noted in the septet system. We find, in addition, the combination $4d_i - np_i$, that is to say, series which are principal to the diffuse series. In the following tables are given the values published by Fraülein Gieseler on Rowland's standard, because she has been able to express the term sequences by formulæ of the Ritz type. The fundamental term of the quintet system is again an *s*-term 4^5_{12}, which has the value 46948·48, expressed in wave-numbers. We may first consider the single *s*-term, the first three-fold *p*-term, and the five-fold *d*- and *f*-terms, and by their combinations we have five series shown in Tables LXIX. and LXX.

In Table LXIX. each component line is represented first by its intensity, secondly by its wave-length, and thirdly by its wave-number. As will be seen the $4d$-terms (4^5_{3i}) are very large, the largest being 46790·87 which is smaller than the *s*-term by only 157·61, and we have as a result a principal series $4d_i - np_i$ as given in Table LXX.

TABLE LXIX.

SHARP SERIES, $4^5_{2i} - n^5_{12}(4p_i - ns)$.

$i = 3, 2, 1.$

$4^5_{23} = 27754{\cdot}69, \quad 4^5_{22} = 27745{\cdot}93, \quad 4^5_{21} = 27740{\cdot}28.$

λ in R.A.	Int.	ν.	$\Delta\nu$.	n.	n^5_{12}.
— 5208·60	12	19193·79	8·76		
— 5206·22	12	19202·55	5·65	4	46948·48
— 5204·69	12	19208·20			
9010·30	6	11095·37	8·80		
9017·45	5	11086·58	5·64	5	16659·18
9022·04	4	11080·92			
5212·38	2	19179·87	8·83		
5214·78	1	19171·04	5·62	6	8574·86
5216·30	0	19165·42			
4436·65	1	22533·31	8·61		
4438·35	0	22524·70	5·63	7	5221·27
4439·46	0	22519·07			

PRINCIPAL SERIES, $4^5_{12} - n^5_{2i}(4s - np)$.

$i = 3, 2, 1.$

$4^5_{12} = 46948{\cdot}48.$

λ in R.A.	Int.	ν.	$\Delta\nu$.	n.	n^5_{2i}.
5208·60	12	19193·79	8·76		27754·69
5206·22	12	19202·55	5·65	4	27745·93
5204·69	12	19208·20			27740·28
3192·28	2*n*	31316·65	—	5	15631·83
2710·56	2	36882·00	—	6	10066·48
2532·72	1	39471·56	—	7	7476·92

TABLE LXIX.—*Continued.*

DIFFUSE SERIES, $4^5_{2i} - n^5_{3i}(4p_i - nd_i)$.

$i = 3, 2, 1.$ $i = 4, 3, 2, 1, 0.$

$4^5_{23} = 27754{\cdot}69,$ $4^5_{22} = 27745{\cdot}93,$ $4^5_{21} = 27740{\cdot}28.$

			$\Delta\nu$.	n.	n^5_{3i}.
12 − 5410·00 18479·27				4	46233·96
10 − 5348·52 18692·26	10 5346·00 18700·47		212·72		46446·68
7 − 5300·93 18860·03	10 5298·28 18868·28	10 5296·87 18873·91	167·69		46614·37
	8 − 5265·89 18984·95	10 5264·33 18990·58	116·50		46730·87
		8 − 5247·74 19050·59	60·00		46790·87
1 5295·84 18877·58				5	8877·11
3 5308·61 18832·18	2 5310·95 18828·88		45·17		8922·28
1 5317·52 18800·60	0 5319·99 18791·91	1 5321·44 18786·75	31·60		8953·88
	1 5325·13 18773·77	1 5326·74 18768·06	18·31		8972·19

TABLE LXX.

PRINCIPAL SERIES TO THE DIFFUSE SERIES, $4^5_{3i} - n^5_{2i}$.

$i = 4, 3, 2, 1, 0.$ $i = 3, 2, 1.$

$4^5_{34} = 46233{\cdot}96,$ $4^5_{33} = 46446{\cdot}68,$ $4^5_{32} = 46614{\cdot}37,$ $4^5_{31} = 46730{\cdot}87,$
$4^5_{30} = 46790{\cdot}87.$

					n	n^5_{2i}.
10 5410·00 18479·27	10 5348·52 18692·26	10 5300·93 18860·02			4	27754·49
	10 5346·00 18700·47	10 5298·28 18868·28	8 5265·89 18984·95		8·42	27746·07
		10 5296·87 18873·91	10 5264·33 18990·58	8 5247·74 19050·59	5·74	27740·33

2	2	2*u*	0*u*	(Calc.)		
3266·68	3244·27	3226·66	3214·62			
30602·65	30814·93	30982·56	31099·07	31159·20	5	15631·67
1	1	(Calc.)	(Calc.)	(Calc.)		
2764·10	2747·95					
36167·67	36380·17	36547·97	36664·47	36724·47	6	10066·40

FUNDAMENTAL SERIES, $4^5_{3i} - n^5_{4i}$.

$i = 4, 3, 2, 1, 0.$ $i = 5, 4, 3, 2, 1.$

$4^5_{34} = 46233{\cdot}96$, $4^5_{33} = 46446{\cdot}68$, $4^5_{32} = 46614{\cdot}37$, $4^5_{31} = 46730{\cdot}87$,

$4^5_{30} = 46790{\cdot}87$.

						n^5_{4i}. $i = 5, 4, 3, 2, 1$.
10						
4351·95					*n*.	
22971·86					4	23262·10
8	10			174·01		
4385·15	4344·67					
22798·06	23010·35					23436·11
4	8	8		141·03		
4412·42	4371·45	4429·62				
22657·04	22869·43	23037·12				23577·14
	5	8	5	106·65		
	4391·92	4359·80	4337·72			
	22762·81	22930·52	23047·21			23683·79
		6	8	8	71·40	
		4373·42	4351·22	4339·89		
		22859·07	22975·72	23035·75		23755·19
3						
3021·68						
33084·75					5	13149·21
3	2			168·85		
3037·16	3017·69					
32916·07	33128·49					13318·04
(Calc.)	3	2		138·74		
	3030·36	3015·05				
32777·18	32990·01	33157·49				13456·78
			3	114·73		
	(Calc.)	(Calc.)	3			
			3014·88			
	32875·17	33042·86	33159·36			13571·51
		2	2	2	64·98	
		3031·46	3020·83	3015·31		
		32977·94	33094·06	33154·63		13636·49

TABLE LXX.—*Continued.*

2						
2684·82						
37235·62					6	8998·34
1	3			157·96		
2696·25	2680·89					
37077·83	37290·20					9156·30
1	3	3		131·20		
2705·83	2690·35	2678·25				
36946·45	37159·12	37326·94				9287·50
	0*u*	2	(Calc.)	85·24		
	2696·51	2684·41				
	37074·26	37241·31	37358·13			9372·74
		(Calc.)	2	0	67·64	
			2680·83	2676·54		
		37173·99	37290·20	37350·78		9440·38

We may now consider the second three-fold p-term which may be denoted by the symbol n^{5a}_{2i}. This term is shifted relatively to the first p-term (n^5_{2i}), dealt with in the preceding tables, by $\Delta\nu = 3037{\cdot}03$. The combination of this new p-term and the sharp and diffuse terms are shown in Table LXXI.

TABLE LXXI.

SHARP SERIES, $4^{5a}_{2i} - n^5_{12}$.

$i = 3, 2, 1.$

$4^{5a}_{23} = 24717{\cdot}86$, $4^{5a}_{22} = 24957{\cdot}77$, $4^{5a}_{21} = 25121{\cdot}52$.

λ in R.A.	Int.	ν.	$\Delta\nu$.	n.	n^5_{12}.
− 4497·03	7	22230·62			
			239·93		
− 4546·22	8	21990·69		4	46948·48
			163·73		
− 4580·22	8	21826·96			

PRINCIPAL SERIES, $4^5_{12} - n^{5a}_{2i}$, $4^5_{12} = 46948{\cdot}48$.

$i = 3, 2, 1.$

λ in R.A.	Int.	ν.	$\Delta\nu$.	n.	n^{5a}_{2i}.
					$i = 3, 2, 1.$
4497·03	7	22230·62			24717·86
			239·91		
4546·22	8	21990·69		4	24957·77
			163·73		
4580·22	8	21826·96			25121·52
2988·78	3	33449·18			13499·30
			60·64		
2994·18	2	33388·54		5	13559·94
			52·65		
2995·91	3	33335·89			13612·59
	(Calc.)	37767·92			9164·98
			15·50		
		37760·04		6	9180·56
			7·88		
		37783·5			9188·44

PRINCIPAL SERIES TO DIFFUSE SERIES, $4^5_{3i} - n^{5a}_{2i}$.

$i = 4, 3, 2, 1, 0.$ $i = 3, 2, 1.$

$4^5_{34} = 46233{\cdot}96$, $4^5_{33} = 46446{\cdot}68$, $4^5_{32} = 46614{\cdot}37$, $4^5_{31} = 46730{\cdot}87$, $4^5_{30} = 46790{\cdot}87$.

					$\Delta\nu$.	n.	n^{5a}_{2i}.
8	7	6					
4646·35	4600·93	4665·63					
21516·34	21728·79	21896·50				4	24717·79
	9	8	8		240·14		
	4652·34	4616·30	4591·57				
	21488·65	21656·41	21773·07				24957·93
		9	8	7	163·64		
		4651·46	4626·36	4613·54			
		21492·72	21609·33	21669·36			25121·57
5	3	2					
3053·99	3034·30	3018·92					
32734·73	32947·08	33114·99				5	13499·40
	2	4	4		60·65		
	3029·89	3024·47	3013·84				
	32886·62	33054·35	33170·80				13560·05
		3	3	3	52·47		
		3029·28	3018·61	3013·15			
		33001·77	33118·39	33178·39			13612·52
1	2	2					
2696·83	2681·48	2669·48					
37069·85	37282·04	37449·54				6	9164·53
	1	3	2		16·04		
	2682·62	2670·62	2662·31				
	37266·15	37433·70	37550·36				9180·57
		2	2	1	7·98		
		2671·17	2662·88	2658·62			
		37425·82	37542·32	37602·44			9188·55

As already stated there are yet two more three-fold p-terms, which we may denote by n^{5b}_{2i} and n^{5c}_{2i} respectively. In the case of the former we have the sharp series as shown in Table LXXII.

TABLE LXXII.

SHARP SERIES, $n^{5b}_{2i} - n^5_{12}$.

i 3, 2, 1.

$n^{5b}_{23} = 10283{\cdot}29$, $n^{5b}_{22} = 10355{\cdot}85$, $n^{5b}_{21} = 10416{\cdot}93$.

λ in R.A.	Int.	ν.	$\Delta\nu$.	n.	n^5_{12}.
— 2726·60	5	36665·19			
— 2732·00	5	36592·63	72·56	4	46948·48
— 2736·57	4	36531·55	61·08		
15680·50	3	6375·44			
15861·60	3	6302·67	72·58	5	16658·57

With only two terms it is not possible to fix the value of n for the principal terms, but if these terms obey a Ritz formula the magnitude of the term given in the above table suggests that $n = 5$. If this is the case there should exist a p-term with $n = 4$ and a magnitude of about 20700. We should expect therefore a strong principal triplet $4^5_{12} - 4^{5b}_{2i}$ at about $\nu = 46948{\cdot}5 - 20700 = 26248{\cdot}5$, but this has not been found. On the other hand, a complex triplet occurs which would seem to be due to the combination $4^5_{3i} - 4^5_{2i}$ and in that case would agree with the above principal term having the total quantum number $n = 5$. Unfortunately the Zeeman resolution of the lines is not known and this conclusion cannot be verified. The two terms are shown in Table LXXIII.

TABLE LXXIII.

PRINCIPAL SERIES TO DIFFUSE SERIES, $4^5_{3i} - n^{5b}_{2i}$.

$i = 4, 3, 2, 1, 0.$

$4^5_{34} = 46233{\cdot}96$, $4^5_{33} = 46446{\cdot}68$, $4^5_{32} = 46614{\cdot}37$, $4^5_{31} = 46730{\cdot}87$, $4^5_{30} = 46790{\cdot}87$.

					$\Delta\nu$.	n.	n^{5b}_{2i}.
3	2	5					
3853·34	3822·20	3797·84					
25944·30	26155·62	26323·41				4	20291·01
	4	1	2		61·01		
	3831·15	3806·70	3789·85				
	26094·53	26262·16	26378·89				20352·02
		3	5	4	55·54		
		3814·74	3797·84	3789·00			
		26206·75	26323·41	26383·27			20407·56
8	3	1					
2780·79	2764·45	2751·69					
35950·66	36163·79	36330·74				5	10283·26
	6	4	3u		72·95		
	2770·01	2757·19	2748·38				
	36090·53	36258·28	36374·48				10356·21
		3	3	3μ	66·72		
		2761·85	2752·96	2748·38			
		36197·12	36313·99	36374·48			10416·93

Assuming that the allocation in Table LXXIII. is correct, the difference between the p^a- and p^b-terms is $\Delta\nu = 4426{\cdot}78$.

Finally, we have the fourth three-fold p-term which we denoted by n^{5c}_{2i}, but as only two triplets have been identified which involve this term we have no information as to the value of n. The values are given in Table LXXIV.

TABLE LXXIV.

PRINCIPAL SERIES, $4^5_{12} - n^{5c}_{2i}$.

$i = 3, 2, 1.$

λ in R.A.	Int.			n^{5c}_{2i}.
2544·82	3	39283·93	88·94	7664·55
2539·07	2	39372·87	54·58	7575·61
2535·37	2	39427·48		7521·03

PRINCIPAL SERIES TO DIFFUSE SERIES, $4^5_{3i} - n^{5c}_{2i}$.

$i = 4, 3, 2, 1, 0.$ $i = 3, 2, 1.$

				$\Delta\nu$.	n^{5c}_{2i}.
3	2	1			
2591·94	2577·75	2566·64			
38569·83	38782·09	38950·06			7664·55
	2	2	1	89·10	
	2571·84	2560·79	2553·14		
	38871·33	39039·02	39155·95		7575·61
		2	2	1	54·34	
		2557·23	2549·60	2545·72		
		39093·35	39210·30	39270·05		7521·03

In addition to the foregoing combinations, there are three other sets of *d*-terms which combine with the normal *d*-terms used in the above tables. These new *d*-terms we may denote by the symbols n^{5a}_{3i}, n^{5b}_{3i}, and n^{5c}_{3i}, respectively, where $i = 4, 3, 2, 1, 0$ in each case. The three multiplets given by the combinations are set forth in Table LXXV., which is taken from Fraülein Gieseler's first paper.

TABLE LXXV.

FIRST MULTIPLET, $4^5_{3i} - n^{5a}_{3i}$.

$i = 4, 3, 2, 1, 0.$

$4^5_{34} = 46233{\cdot}96$, $4^5_{33} = 46446{\cdot}68$, $4^5_{32} = 46614{\cdot}37$, $4^5_{31} = 46730{\cdot}87$, $4^5_{30} = 46790{\cdot}87$.

9	6					
3919·31	3886·94					
25507·60	25720·03					$n^{5a}_{34} = 20726{\cdot}42$
5	7	6			144·49	
3941·64	3908·90	3883·41				
25363·14	25575·51	25743·41				$n^{5a}_{33} = 20870{\cdot}89$
	8	6	6		129·66	
	3928·79	3903·09	3885·36			
	25446·07	25613·57	25730·49			$n^{5a}_{32} = 21000{\cdot}50$
		7	5	6	118·24	
		3921·19	3903·31	3894·18		
		25495·38	25612·20	25672·22		$n^{5a}_{31} = 21118{\cdot}72$
			6		85·52	
			3916·38			
			25526·68			$n^{5a}_{30} = 21204{\cdot}16$

TABLE LXXV.—*Continued.*

This multiplet is the second of those discovered by Catalan.

SECOND MULTIPLET, $4^5_{3i} - n^{5b}_{3i}$.

$i = 4, 3, 2, 1, 0.$

3	3					
2986·59	2967·76					
33473·36	33685·80					$n^{5b}_{34} = 12760{\cdot}65$
3	3	4			206·97	
3005·17	2986·11	2971·22				
33266·47	33478·75	33646·69				$n^{5b}_{33} = 12967{\cdot}61$
	3	3	3		167·18	
	3001·10	2985·98	2975·60			
	33311·57	33480·31	33597·29			$n^{5b}_{32} = 13134{\cdot}15$
		3	2	4	119·87	
		2996·69	2986·25	2980·91		
		33360·57	33472·29	33537·25		$n^{5b}_{31} = 13253{\cdot}65$
			3		64·54	
			2992·02			
			33412·75			$n^{5b}_{30} = 13318{\cdot}09$

THIRD MULTIPLET, $4^5_{3i} - n^{5c}_{3i}$.

$i = 4, 3, 2, 1, 0.$

3	2					
2889·37	2871·75					
34599·68	34812·03					$n^{5c}_{34} = 11634{\cdot}38$
2	2	2			260·06	
2911·25	2893·36	2879·38				
34339·60	34551·99	34719·69				$n^{5c}_{33} = 11894{\cdot}52$
	3	2	1		209·54	
	2911·01	2896·86	2887·10			
	34342·43	34510·25	34626·88			$n^{5c}_{32} = 12104{\cdot}02$
		2	1	2	145·92	
		2909·17	2899·31	2894·28		
		34364·26	34480·97	34540·97		$n^{5c}_{31} = 12249{\cdot}99$
			2		74·49	
			2905·59			
			34406·48			$n^{5c}_{30} = 12324{\cdot}36$

This completes the list of lines which arise from combinations of the terms of the quintet system of neutral chromium as far as the series relationships have been worked out. It was shown previously that the *s*-terms in the septet system can be expressed by a Ritz equation. Fraülein Gieseler gives some interesting facts as regards the terms of the quintet system which may be recorded here. In the first place, the *s*-terms (n^5_{12}) can be fairly accurately expressed by the equation

$$n^5_{12} = \frac{N_{cr}}{[n + s^5 + \sigma^5(ns^5)]^2},$$

where $N_{cr} = 109735{\cdot}95$, $s^5 = 0{\cdot}5882$, and $\sigma^5 = -1{\cdot}289 \times 10^{-6}$, with the following errors (obs. — calc.) :—

$n =$	4	5	6	7
	− 70·5	+ 2·52	− 0·86	− 6·62

The principal terms (n^5_{2i}) cannot be directly expressed by a Ritz equation, but if a constant number be subtracted from them they can then be so expressed with the exception of the first term which deviates from the calculated value by an amount which is approximately equal to the constant. This is analogous to the case of neon as noted by Paschen.[1] The differences (obs. — calc.) are given in Table LXXVI., the Ritz equation being

$$n^5_{2i} \text{ red.} = \frac{N_{cr}}{[n + p^5_i + \pi^5_i(np^5_i)]^2}.$$

TABLE LXXVI.

$n^5_{2i} - A = n^5_{2i}$ red., $N_{cr} = 109735{\cdot}95$, $A = 2929$.

$n =$	4	5	6	7
		$p^5_3 = 0{\cdot}8978$,	$\pi^5_3 = 3{\cdot}252 \times 10^{-6}$	
	− 2937·11	− 0·27	− 0·03	+ 1·12
		$p^5_2 = 0{\cdot}8973$,	$\pi^5_2 = 3{\cdot}2856 \times 10^{-6}$	
	− 2934·87	− 1·17	− 1·15	− 0·05
		$p^5_1 = 0{\cdot}8973$,	$\pi^5_1 = 3{\cdot}2896 \times 10^{-6}$	
	− 2937·72	− 0·67	− 0·97	+ 0·33

It will be noted that the n^5_{2i} and n^{5c}_{2i} terms are reversed terms (see p. 139). A relationship somewhat similar to the above exists with the n^{5a}_{2i} terms, but in this case there is no divergence in the values for the first term, as may be seen from Table LXXVII.

TABLE LXXVII.

$n^{5a}_{2i} - A = n^{5a}_{2i}$ red.

$n =$	4	5	6
	A = 3053·36,	$p^{5a}_3 = 0{\cdot}2323$,	$\pi^{5a}_3 = 8{\cdot}454 \times 10^{-7}$
	+ 0·20	− 0·26	+ 0·30
	A = 3033·26,	$p^{5a}_2 = 0{\cdot}22041$,	$\pi^{5a}_2 = 7{\cdot}726 \times 10^{-7}$
	+ 2·41	− 1·12	+ 0·31
	A = 3001	$p^{5a}_1 = 0{\cdot}2052$	$\pi^{5a}_1 = 9{\cdot}9698 \times 10^{-7}$
	1·28	− 0·11	− 0·04

[1] *Ann. der Phys.*, **63**, 20 (1920).

A relation similar to the last also exists with the fundamental terms as set forth in Table LXXVIII.

TABLE LXXVIII.

$n^5_{4i} - A = n^5_{4i}$ red.

n = 4	5	6
A = 2967, − 6·10	f_5 = 0·23986, − 1·99	$\phi_5 = 4{\cdot}193 \times 10^{-6}$ − 0·92
A = 3110·5, ± 0·11	f_4 = 0·23361, − 0·06	$\phi_4 = 4{\cdot}426 \times 10^{-6}$ 0·00
A = 3231·54, + 0·9	f_3 = 0·22908, + 0·24	$\phi_3 = 4{\cdot}587 \times 10^{-6}$ + 0·18
A = 3278, + 3·29	f_2 = 0·21031, + 0·91	$\phi_2 = 5{\cdot}335 \times 10^{-6}$ − 1·16
A = 3347, + 0·59	f_1 = 0·21157, − 0·21	$\phi_1 = 5{\cdot}258 \times 10^{-6}$ + 0·22

In addition to the combination between the septet terms and between the quintet terms, there also exist combinations between septet and quintet terms. Five of these combinations were recognised by Catalan and one additional combination by Fraülein Gieseler.

In the foregoing description of the multiplets in the arc spectrum of chromium reference was made to the fact that the fundamental orbit is the 4*s*-orbit of the septet system and that this term in wave-numbers has the value 54541·26. It follows from this that the absorption spectrum of metallic chromium vapour should show the lines of the principal series which in the emission spectrum are given by the transition $4s - np_i$. As there are in the case of chromium two triplet *p*-terms, the absorption spectrum should show the two triplets $4s - 4p_i$ and $4s - 4p_i^a$, which consist of the lines at $\lambda = 4289{\cdot}92$, 4275·01, 4254·52, and 3605·49, 3593, 3578·81, respectively. The absorption spectrum of chromium vapour was observed by Fraülein Gieseler and Dr. W. Grotrian,[1] who used a quartz tube heated to 1250°, and these two triplets were the only lines observed. It might have been expected that the principal triplet of the quintet system would be observed as absorption lines, but these lines are weak in the emission spectrum, and consequently we may conclude that the probability of these transitions taking place is too small for these lines to appear in the absorption spectrum at such low densities of chromium vapour as are obtained at 1250°. These observations completely confirm the allocation of the chromium lines by Catalan and by Fraülein Gieseler.

As will be seen from the foregoing account of the work on the multiplets of chromium and manganese, the position arrived at is one of great interest. At one end of a horizontal row of the periodic

[1] *Zeitsch. für Phys.*, **22**, 245 (1924).

table we have potassium and calcium, followed by scandium, titanium, vanadium, chromium, manganese, and iron. Whereas potassium exhibits doublet terms and calcium exhibits singlet and triplet terms, the question at once arises as to the nature of the spectral terms of the three elements lying between these two and chromium with its quintet and septet terms and manganese with its quartet, sextet, and octet terms. It is not surprising that these three elements, scandium, titanium, and vanadium, were at once examined for the existence of multiplets which as a matter of fact were readily identified. It is of great interest to note that odd and even multiplicities alternate, since scandium shows doublet and quartet terms, titanium shows triplet and quintet terms, and vanadium shows quartet and sextet terms. There is no need to enter into the details of this work and reference to the various publications will be sufficient.[1]

Of the elements in the above-mentioned horizontal row of the periodic table there remains to be considered only the case of iron, which by the scheme of alternation should show terms of uneven multiplicities, since this element follows after manganese, the spectral terms of which belong to the even systems of multiplicities. The first evidence of multiplet structure in the arc spectrum of iron was obtained by Walters [2] who succeeded in identifying twenty multiplets. Subsequently two masterly papers have been published by Laporte [3] who discovered altogether fifty-three multiplets and was able to prove the existence of triplet, quintet, and septet terms. Laporte proved that these multiplets conformed to Landé's rule as regards the interval ratios and to the rule of intensities as enunciated by Sommerfeld and by Landé, and confirmed by Burger and Dorgelo. Then again, the whole group of multiplets conforms to the rules of the Zeeman effect as established by Landé and to be described in Chapter II. Furthermore the lines which are grouped together in multiplets are, in general, lines of the same temperature class or at any rate of two neighbouring classes. Laporte has been able to identify the various terms involved and to determine their relative magnitudes. Lastly, he has been able definitely to allocate 600 of the iron arc lines, that is to say, about one-quarter of the total number. We may discuss Laporte's two papers separately, and commence with the first.

The complexity of the iron spectrum is greater than that of the chromium spectrum, since in only very few cases was more than one term of any series identified. Except for these instances each multiplet forms a single member of a series.

As has previously been explained the transitions in the azimuthal quantum number k are restricted by the selection principle to $\Delta k = \pm 1$,

[1] Scandium: Catalan, *Anales Soc. Espan. Fis. y Quim.*, **20**, 606 (1922); **21**, 464 (1923).
Titanium: C. C. Kiess and H. F. Kiess, *J. Wash. Acad. Sci.*, **13**, 270 (1923).
Vanadium: Meggers, *ibid.*, **13**, 317 (1923); Laporte, *Phys. Zeitsch.*, **24**, 510 (1923).

[2] *J. Wash. Acad. Sci.*, **13**, 243 (1923).

[3] *Zeitsch. für Phys.*, **23**, 135 (1924); **26**, 1 (1924).

but this was deduced for electronic orbits of the type of those of the alkaline and alkaline-earth metals, which are not present in the deeper orbits of the iron atom. It is not surprising therefore to find amongst the numerous multiplets of the iron spectrum two due to the combination (pf) which with $\Delta k = 2$ contravenes the ordinarily accepted selection principle.

It will be remembered that in the cases of chromium and manganese several terms, *e.g.* *d*-terms, with the same azimuthal quantum number were identified and that combinations occurred between some of these and not between others. In all probability those terms with equal azimuthal quantum number which combine together belong to different states of the atomic trunk, and it is necessary to differentiate between the two types. The German scientists, following the lead of Götze,[1] speak of them as *ungestrichene* and *gestrichene Terme* (*e.g.*, *d* and *d'*), and in order to avoid the somewhat ambiguous literal translation we may write them as *d* and *d**. The contravention of the selection principle has already been mentioned (see p. 117) and will be discussed below.[2]

It is important to note that, although the selection principle is disobeyed in two cases as regards the azimuthal quantum number, Sommerfeld's selection principle for the inner quantum number is rigidly obeyed, according to which $\Delta i = \pm 1$ or 0, and that the transition $i \rightarrow i = 0 \rightarrow 0$ is forbidden (Landé).

Laporte used three criteria in the allocation of lines to each multiplet :—

1. Sommerfeld's rule of intensities.
2. Landé's rule of interval ratios.
3. Zeeman effect.

As was shown above the orientation of the inner quantum numbers is given by the relation

$$r = 2i_s + 1,$$

where i_s is the true inner quantum number (Sommerfeld) of the sharp term, and $r = 1, 2, 3$, etc., for singlet, doublet, triplet, etc., terms.

We may adopt Laporte's symbols for the various terms, since the values of the total quantum numbers n have not yet been determined. The terms of the quintet system are denoted by p, d, f, g, and those of the triplet system by P, D, F, G. The total number of terms given in the first paper are as follows :—

Quintet system, p^1, p^2, d^1, d^2, d^{1*}, d^{2*}, d^{3*}, f^1, f^2, f^3, f^{1*}, g^{1*},
Triplet system, P^1, D^{1*}, F^1, F^{1*}, G^{1*},

from which the combinations shown in Table LXXIX. have been found.

[1] *Ann. der Phys.*, **66**, 285 (1921).

[2] See below, pp. 202 and 290.

TABLE LXXIX.

1	(d^1p^1)	10	$(f^{1*}d^{2*})$	18	$(d^{1*}d^2)$	26	$(f^{1*}F^1)$
2	(d^1p^2)	11	$(f^{1*}d^{3*})$	19	(f^1d^2)	27	$(f^{1*}G^{1*})$
3	(d^1d^{1*})	12	$(f^{1*}f^1)$	20	$(F^{1*}D^{1*})$	28	$(f^{1*}P^1)$
4	(d^1d^{2*})	13	$(f^{1*}f^2)$	21	$(F^{1*}D^{2*})$	29	$(F^{1*}d^{3*})$
5	(d^1d^{3*})	14	$(f^{1*}f^3)$	22	$(F^{1*}F^1)$	30	$(F^{1*}f^2)$
6	(d^1f^1)	15	$(f^{1*}g^{1*})$	23	$(F^{1*}G^{1*})$	31	$(F^{1*}g^{1*})$
7	(d^1f^2)	16	$(f^{1*}p^2)$	24	(d^1P^1)	32	$(\delta\delta^*)$
8	(d^1f^3)	17	(p^1d^2)	25	(d^1D^{1*})	33	$(\pi\delta)$
9	$(f^{1*}d^{1*})$						

In Tables LXXX. to LXXXIII. are set forth the first set of multiplets. In each case there are given in order the wave-length, intensity, temperature class, wave-number, and the term combination of the lines composing the multiplets. There are also given at the end of each multiplet the values of the interval ratios as observed and calculated by Landé's rule.

TABLE LXXX.

QUINTET SYSTEM.

MULTIPLET NO. I.

Combination $d_i^1 - p_i^1$, $\Delta k = +1$.

3476·71	40	I.	28754·6	$d_0^1p_1^1$	3440·99	75R	I.	29053·2	$d_3^1p_2^1$
3465·86	60r	I.	28844·6	$d_1^1p_1^1$	3526·07	20	I.	28352·1	$d_2^1p_3^1$
3443·88	50r	I.	29028·8	$d_2^1p_1^1$	3490·58	100r	I.	28640·3	$d_3^1p_3^1$
3497·84	40	I.	28580·9	$d_1^1p_2^1$	3440·61	150R	I.	29056·3	$d_4^1p_3^1$
3475·45	70r	I.	28765·1	$d_2^1p_2^1$					

Interval ratios, Δd^1 89·9 : 184·1 : 288·1 : 416·0 — {0·9 : 1·8 : 2·7 : 4 obs. / 1·0 : 2·0 : 3·0 : 4 calc.

Δp^1 263·7 : 412·9 = {1·9 : 3 obs. / 2·0 : 3 calc.

MULTIPLET NO. II.

Combination $d_i^1 - p_i^2$, $\Delta k = +1$.

2744·07	10	II.	36431·44	$d_0^1p_1^2$	2720·91	40r	II.	36741·55	$d_3^1p_2^2$
2737·31	20r	II.	36521·39	$d_1^1p_1^2$	2772·11	1	III.	36062·94	$d_2^1p_3^2$
2723·58	15	II.	36705·50	$d_2^1p_1^2$	2750·15	25R	II.	36351·00	$d_3^1p_3^2$
2756·33	20	I.	36269·38	$d_1^1p_2^2$	2719·04	60R	II.	36766·84	$d_4^1p_3^2$
2742·41	30r	II.	36453·53	$d_2^1p_2^2$					

Interval ratios, Δd^1 as in No. I.

Δp^2 252·0 : 390·6 — {1·8 : 3 obs. / 2·0 : 3 calc.

TABLE LXXX.—*Continued.*

MULTIPLET No. III.

Combination $d_i^{\mathrm{I}} - d_i^{\mathrm{I}*}$ $\Delta k = 0$.

3895·66	25*r*	I.	25662·35	$d_1^{\mathrm{I}} d_0^{\mathrm{I}*}$	3856·37	100R	I.A	25923·77	$d_3^{\mathrm{I}} d_2^{\mathrm{I}*}$
3920·26	20*r*	I.	25501·31	$d_0^{\mathrm{I}} d_1^{\mathrm{I}*}$	3930·30	25R	I.	25436·14	$d_2^{\mathrm{I}} d_3^{\mathrm{I}*}$
3906·48	8	I.	25591·23	$d_1^{\mathrm{I}} d_1^{\mathrm{I}*}$	3886·29	40R	I.	25724·24	$d_3^{\mathrm{I}} d_3^{\mathrm{I}*}$
3878·58	100R	II.	25775·35	$d_2^{\mathrm{I}} d_1^{\mathrm{I}*}$	3824·44	100R	I.A	26140·19	$d_4^{\mathrm{I}} d_3^{\mathrm{I}*}$
3927·93	30R	I.	25451·45	$d_1^{\mathrm{I}} d_2^{\mathrm{I}*}$	3922·92	25R	I.	25484·03	$d_3^{\mathrm{I}} d_4^{\mathrm{I}*}$
3899·71	30R	I.	25635·67	$d_2^{\mathrm{I}} d_2^{\mathrm{I}*}$	3859·91	300R	I.	25900·00	$d_4^{\mathrm{I}} d_4^{\mathrm{I}*}$

Interval ratios, Δd^{I} as in No. I.

$\Delta d^{\mathrm{I}*}$ 71·1 : 139·7 : 199·5 : 240·2 = {1·2 : 2·3 : 3·3 : 4 obs. / 1·0 : 2·0 : 3·0 : 4 calc.

MULTIPLET No. IV.

Combination $d_i^{\mathrm{I}} - d_i^{2*}$ $\Delta k = 0$.

3008·14	60R	I.	33233·45	$d_1^{\mathrm{I}} d_0^{2*}$	2994·43	100R	I.	33385·54	$d_3^{\mathrm{I}} d_2^{2*}$
3025·85	50R	I.	33039·01	$d_0^{\mathrm{I}} d_1^{2*}$	3047·61	100R	I.	32803·10	$d_2^{\mathrm{I}} d_3^{2*}$
3017·63	15*r*	I.A	33128·96	$d_1^{\mathrm{I}} d_1^{2*}$	3021·08	150R	I.	33091·17	$d_3^{\mathrm{I}} d_3^{2*}$
3000·95	100R	I.	33313·08	$d_2^{\mathrm{I}} d_1^{2*}$	2983·57	125R	I.	33507·13	$d_4^{\mathrm{I}} d_3^{2*}$
3037·39	80R	I.	32913·43	$d_1^{\mathrm{I}} d_2^{2*}$	3059·09	100R	I.	32679·98	$d_3^{\mathrm{I}} d_4^{2*}$
3020·50	100R	II.	33097·53	$d_2^{\mathrm{I}} d_2^{2*}$	3020·64	200R	I.	33095·93	$d_4^{\mathrm{I}} d_4^{2*}$

Interval ratios, Δd^{I} as in No. I.

Δd^{2*} 104·5 : 215·5 : 294·4 : 411·2 = {1·0 : 2·1 : 2·9 : 4 obs. / 1·0 : 2·0 : 3·0 : 4 calc.

MULTIPLET No. V.

Combination $d_i^{\mathrm{I}} - d_i^{3*}$ $\Delta k = 0$.

2524·29	8*r*	II.	39603·02	$d_1^{\mathrm{I}} d_0^{3*}$	2510·84	15R	II.	39815·25	$d_3^{\mathrm{I}} d_2^{3*}$
2535·61	8*r*	III.	39426·34	$d_0^{\mathrm{I}} d_1^{3*}$	2545·98	10*r*	III.	39265·71	$d_2^{\mathrm{I}} d_3^{3*}$
2529·83	3	III.	39516·46	$d_1^{\mathrm{I}} d_1^{3*}$	2527·44	15*r*	II.	39553·82	$d_3^{\mathrm{I}} d_3^{3*}$
2518·11	12*r*	II.	39700·36	$d_2^{\mathrm{I}} d_1^{3*}$	2501·14	20R	II.	39969·72	$d_4^{\mathrm{I}} d_3^{3*}$
2540·98	10R	III.	39343·20	$d_1^{\mathrm{I}} d_2^{3*}$	2549·62	10*r*	III.	39209·92	$d_3^{\mathrm{I}} d_4^{3*}$
2529·14	3	—	39527·20	$d_2^{\mathrm{I}} d_2^{3*}$	2522·86	40R	II.	39625·63	$d_4^{\mathrm{I}} d_4^{3*}$

Interval ratios, Δd^{I} as in No. I.

Δd^{3*} 86·6 : 173·2 : 261·5 : 344·0 = {1·0 : 2·0 : 3·0 : 4 obs. / 1·0 : 2·0 : 3·0 : 4 calc.

Multiplet No. VI.

Combination $d^{\mathrm{I}}_i - f^{1}_i$ $\Delta k = -1$.

3745·90	80R	I.A	26688·31	$d^{\mathrm{I}}_0 f^{\mathrm{I}}_1$	3745·56	150R	I.	26690·69	$d^{\mathrm{I}}_2 f^{\mathrm{I}}_3$
3733·32	80R	I.A	26778·22	$d^{\mathrm{I}}_1 f^{\mathrm{I}}_1$	3705·57	100R	I.	26978·76	$d^{\mathrm{I}}_3 f^{\mathrm{I}}_3$
3707·83	20r	I.	26962·43	$d^{\mathrm{I}}_2 f^{\mathrm{I}}_1$	3649·31	20r	I.A	27394·67	$d^{\mathrm{I}}_4 f^{\mathrm{I}}_3$
3748·26	125R	I.	26671·45	$d^{\mathrm{I}}_1 f^{\mathrm{I}}_2$	3737·14	200R	I.	26750·88	$d^{\mathrm{I}}_3 f^{\mathrm{I}}_4$
3722·57	100R	I.A	26855·57	$d^{\mathrm{I}}_2 f^{\mathrm{I}}_2$	3679·92	100R	I.A	27166·82	$d^{\mathrm{I}}_4 f^{\mathrm{I}}_4$
3683·06	20r	I.A	27143·66	$d^{\mathrm{I}}_3 f^{\mathrm{I}}_2$	3719·94	300R	I.	26874·53	$d^{\mathrm{I}}_4 f^{\mathrm{I}}_5$

Interval ratios, Δd^{1} as in No. I.

Δf^{1} 106·7 : 164·9 : 227·9 : 292·3 = { 1·8 : 2·8 : 3·9 : 5 obs. ; 2·0 : 3·0 : 4·0 : 5 calc.

Multiplet No. VII.

Combination $d^{\mathrm{I}}_i - f^{2}_i$ $\Delta k = -1$.

2965·26	20	II.	33714·06	$d^{\mathrm{I}}_0 f^{2}_1$	2973·14	60R	I.	33624·72	$d^{\mathrm{I}}_2 f^{2}_3$
2957·37	30R	II.	33803·97	$d^{\mathrm{I}}_1 f^{2}_1$	2947·88	60R	I.	33912·84	$d^{\mathrm{I}}_3 f^{2}_3$
2941·34	15r	I.	33988·12	$d^{\mathrm{I}}_2 f^{2}_1$	2912·16	20r	I.	34328·72	$d^{\mathrm{I}}_4 f^{2}_3$
2970·11	(?)	I.	33659·02	$d^{\mathrm{I}}_1 f^{2}_2$	2973·24	60R	I.	33623·60	$d^{\mathrm{I}}_3 f^{2}_4$
2953·94	50R	II.	33843·18	$d^{\mathrm{I}}_2 f^{2}_2$	2936·90	60R	I.	34039·53	$d^{\mathrm{I}}_4 f^{2}_4$
2929·01	25r	I.	34131·31	$d^{\mathrm{I}}_3 f^{2}_2$	2966·90	125R	II.	33695·37	$d^{\mathrm{I}}_4 f^{2}_5$

Interval ratios, Δd^{1} as in No. I.

Δf^{2} 144·9 : 218·5 : 289·2 : 344·1 = { 2·1 : 3·2 : 4·2 : 5 obs. ; 2·0 : 3·0 : 4·0 : 5 calc.

Multiplet No. VIII.

Combination $d^{\mathrm{I}}_i - f^{3}_i$ $\Delta k = -1$.

2489·76	15r	II.	40152·42	$d^{\mathrm{I}}_0 f^{3}_1$	2490·66	30R	II.	40137·91	$d^{\mathrm{I}}_2 f^{3}_3$
2484·19	15R	II.	40242·45	$d^{\mathrm{I}}_1 f^{3}_1$	2472·91	6R	II.	40425·96	$d^{\mathrm{I}}_3 f^{3}_3$
2472·88	6R	II.	40426·53	$d^{\mathrm{I}}_2 f^{3}_1$	2447·72	4	II.(?)	40842·01	$d^{\mathrm{I}}_4 f^{3}_3$
2491·16	20R	II.	40129·79	$d^{\mathrm{I}}_1 f^{3}_2$	2488·15	40R	II.	40178·41	$d^{\mathrm{I}}_3 f^{3}_4$
2479·78	20R	II.	40313·95	$d^{\mathrm{I}}_2 f^{3}_2$	2462·65	10r	II.	40594·35	$d^{\mathrm{I}}_4 f^{3}_4$
2462·19	4	III.	40601·94	$d^{\mathrm{I}}_3 f^{3}_2$	2483·28	60R	II.	40257·21	$d^{\mathrm{I}}_4 f^{3}_5$

Interval ratios, Δd^{1} as in No. I.

Δf^{3} 112·6 : 176·0 : 247·6 : 337·1 = { 1·9 : 2·6 : 3·7 : 5 obs. ; 2·0 : 3·0 : 4·0 : 5 calc.

TABLE LXXX.—*Continued.*

MULTIPLET No. IX.

Combination $f_i^{1*} - d_i^{1*}$ $\Delta k = +1$.

5434·53	30	I.	18395·76	$f_1^{1*}d_0^{1*}$	5506·79	18	I.	18154·40	$f_2^{1*}d_3^{1*}$
5455·62	40	I.	18324·66	$f_1^{1*}d_1^{1*}$	5429·70	40	I.	18412·11	$f_3^{1*}d_3^{1*}$
5405·78	40	I.	18493·59	$f_2^{1*}d_1^{1*}$	5328·04	50	I.	18763·40	$f_4^{1*}d_3^{1*}$
5497·52	15	I.	18184·98	$f_1^{1*}d_2^{1*}$	5501·47	12	I.	18171·92	$f_3^{1*}d_4^{1*}$
5446·92	40	I.	18353·90	$f_2^{1*}d_2^{1*}$	5397·14	40	I.	18523·21	$f_4^{1*}d_4^{1*}$
5371·50	50	I.	18611·62	$f_3^{1*}d_2^{1*}$	5269·54	60	I.	18971·72	$f_5^{1*}d_4^{1*}$

Interval ratios, Δd^{1*} as in No. III.

Δf^{1*} 168·9 : 257·7 : 351·3 : 448·5 = { 1·9 : 2·9 : 3·9 : 5 obs. / 2·0 : 3·0 : 4·0 : 5 calc.

MULTIPLET No. X.

Combination $f_i^{1*} - d_i^{2*}$ $\Delta k = +1$.

3849·97	40*r*	II.	25966·89	$f_1^{1*}d_0^{2*}$	3917·19	8	II.	25521·32	$f_2^{1*}d_3^{2*}$
3865·53	40*r*	II.	25862·38	$f_1^{1*}d_1^{2*}$	3878·02	60R	II.	25779·05	$f_3^{1*}d_3^{2*}$
3840·44	60R	II.	26031·30	$f_2^{1*}d_1^{2*}$	3825·89	125R	II.	26130·35	$f_4^{1*}d_3^{2*}$
3898·01	10	II.	25646·86	$f_1^{1*}d_2^{2*}$	3940·89	5	II.	25367·84	$f_3^{1*}d_4^{2*}$
3872·51	60R	II.	25815·77	$f_2^{1*}d_2^{2*}$	3887·05	15	I.	25719·16	$f_4^{1*}d_4^{2*}$
3834·23	80R	II.	26073·50	$f_3^{1*}d_2^{2*}$	3820·43	200R	II.	26167·66	$f_5^{1*}d_4^{2*}$

Interval ratios, Δf^{1*} as in No. IX.

Δd^{2*} as in No. IV.

MULTIPLET No. XI.

Combination $f_i^{1*} - d_i^{3*}$ $\Delta k = +1$.

3091·58	20	II.	32336·56	$f_1^{1*}d_0^{3*}$	3125·66	15	III.	31983·99	$f_2^{1*}d_3^{3*}$
3099·90	15	II.	32249·79	$f_1^{1*}d_1^{3*}$	3100·67	20	II.	32241·78	$f_3^{1*}d_3^{3*}$
3083·75	20	II.	32418·71	$f_2^{1*}d_1^{3*}$	3067·25	30*r*	II.	32593·04	$f_4^{1*}d_3^{3*}$
3116·62	12	III.	32076·65	$f_1^{1*}d_2^{3*}$	3134·11	10	III.	31897·78	$f_3^{1*}d_4^{3*}$
3100·31	20	II.	32245·56	$f_2^{1*}d_2^{3*}$	3099·97	20	II.	32249·05	$f_4^{1*}d_4^{3*}$
3075·72	25*r*	II.	32503·25	$f_3^{1*}d_2^{3*}$	3057·45	40R	II.	32697·50	$f_5^{1*}d_4^{3*}$

Interval ratios, Δf^{1*} as in No. IX.

Δd^{3*} as in No. V.

MULTIPLET No. XII.

Combination $f_i^{I*} - f_i^{I}\ \Delta k = 0.$

5123·73	6	I.	19511·63	$f_1^{I*}f_1^{I}$	4994·13	8	I.	20017·93	$f_4^{I*}f_3^{I}$
5079·74	4	I.	19680·55	$f_2^{I*}f_1^{I}$	5142·93	6	I.	19438·75	$f_3^{I*}f_4^{I}$
5151·92	4	I.	19404·86	$f_1^{I*}f_2^{I}$	5051·64	10	I.	19790·04	$f_4^{I*}f_4^{I}$
5107·45	6	I.	19573·77	$f_2^{I*}f_2^{I}$	4939·69	4	I.	20238·55	$f_5^{I*}f_4^{I}$
5041·08	7	I.	19831·51	$f_3^{I*}f_2^{I}$	5127·36	5	I.	19497·77	$f_4^{I*}f_5^{I}$
5150·85	6	I.	19408·90	$f_2^{I*}f_3^{I}$	5012·07	12	I.	19946·28	$f_5^{I*}f_5^{I}$
5083·34	7	I.	19666·61	$f_3^{I*}f_3^{I}$					

Interval ratios, Δf^{1*} as in No. IX.
Δf^{1} as in No. VI.

MULTIPLET No. XIII.

Combination $f_i^{I*} - f_i^{2}\ \Delta k = 0.$

3767·19	60R	II.	26537·43	$f_1^{I*}f_1^{2}$	3709·25	40R	II.	26952·00	$f_4^{I*}f_3^{2}$
3743·36	40R	II.A	26706·35	$f_2^{I*}f_1^{2}$	3799·55	40R	II.	26311·47	$f_3^{I*}f_4^{2}$
3787·88	30R	II.	26392·53	$f_1^{I*}f_2^{2}$	3749·49	125R	II.	26662·76	$f_4^{I*}f_4^{2}$
3763·79	80R	II.	26561·42	$f_2^{I*}f_2^{2}$	3687·46	40R	I.	27111·27	$f_5^{I*}f_4^{2}$
3727·62	40R	II.	26819·15	$f_3^{I*}f_2^{2}$	3798·51	30R	II.	26318·65	$f_4^{I*}f_5^{2}$
3795·00	40R	II.	26342·98	$f_2^{I*}f_3^{2}$	3734·87	150R	II.	26767·12	$f_5^{I*}f_5^{2}$
3758·23	125R	II.	26600·71	$f_3^{I*}f_3^{2}$					

Interval ratios, Δf^{1*} as in No. IX.
Δf^{2} as in No. VII.

MULTIPLET No. XIV.

Combination $f_i^{I*} - f_i^{3}\ \Delta k = 0.$

3031·64	15	III.	32975·86	$f_1^{I*}f_1^{3}$	2987·29	10	III.	33465·38	$f_4^{I*}f_3^{3}$
3016·20	12	III.	33144·67	$f_2^{I*}f_1^{3}$	3041·75	15	III.	32866·33	$f_5^{I*}f_4^{3}$
3042·03	15	III.	32863·30	$f_1^{I*}f_2^{3}$	3009·58	25*r*	II.	33217·02	$f_4^{I*}f_4^{3}$
3026·47	15	III.	33032·22	$f_2^{I*}f_2^{3}$	2969·48	10	I.	33666·10	$f_5^{I*}f_4^{3}$
3003·03	10	III.	33289·98	$f_3^{I*}f_2^{3}$	3040·43	15	III.	32880·54	$f_4^{I*}f_5^{3}$
3042·67	15	III.	32856·31	$f_2^{I*}f_3^{3}$	2999·52	30R	II.	33329·02	$f_5^{I*}f_5^{3}$
3018·99	15*r*	III.	33114·06	$f_3^{I*}f_3^{3}$					

Interval ratios, Δf^{1*} as in No. IX.
Δf^{3} as in No. VIII.

TABLE LXXX.—*Continued.*

MULTIPLET No. XV.

Combination $f_i^{I*} - g_i^{I*}$ $\Delta k = -1$.

3608·86	80R	I.	27701·70	$f_1^{I*}g_2^{I*}$	3631·46	100R	I.	27529·29	$f_3^{I*}g_4^{I*}$
3586·99	25R	II.	27870·61	$f_2^{I*}g_2^{I*}$	3585·71	20R	II.	27880·57	$f_4^{I*}g_4^{I*}$
3554·12	12	III.A	28128·34	$f_3^{I*}g_2^{I*}$	Calc.	—	—	28329·10	$f_5^{I*}g_4^{I*}$
3618·77	100R	I.	27625·84	$f_2^{I*}g_3^{I*}$	3647·85	100R	I.	27405·65	$f_4^{I*}g_5^{I*}$
3585·32	30R	II.	27883·56	$f_3^{I*}g_3^{I*}$	3589·11	12*r*	III.	27854·18	$f_5^{I*}g_5^{I*}$
3540·71	8	III.A	28234·85	$f_4^{I*}g_3^{I*}$	3581·20	200R	I.	27915·62	$f_5^{I*}g_6^{I*}$

The line at $\lambda = 3581{\cdot}20$ ($\nu = 27915{\cdot}62$) is the only line in that region of the spectrum which could possibly be considered as having its origin in the transition $f_5^{I*} - g_6^{I*}$, but as is obvious its wave-number is entirely out of place. The correct value should be approximately 28424. Great confidence could not be felt in the reality of this g_6^{I*} term were it not for the fact that Laporte finds the intercombination ($F^{1*}g^{1*}$) in which the levels g_2^{I*}, g_3^{I*}, g_4^{I*}, and g_5^{I*} take part. No confirmation can be obtained from this as to the g_6^{I*} level, since the selection principle forbids the combination between it and any level of the F^{1*} term. See, however, Multiplet No. XLVII.

Interval ratios, Δf^{1*} as in No. IX.

$$\Delta g^{1*}\ 244{\cdot}8 : 354{\cdot}3 : 474{\cdot}9 : -61{\cdot}4 = \begin{cases} 2{\cdot}6 : 3{\cdot}7 : 5{\cdot}0 : ? & \text{obs.} \\ 3{\cdot}0 : 4{\cdot}0 : 5{\cdot}0 : 6 & \text{calc.} \end{cases}$$

MULTIPLET No. XVI.

Combination $f_i^{1*} - p_i^2$ $\Delta k = +2$.

3417·27	1	—	29254·81	$f_1^{1*}p_1^2$	3396·98	3	III.A	29429·48	$f_3^{1*}p_2^2$
3397·64	2	III.A	29423·76	$f_2^{1*}p_1^2$	3473·50	1	—	28781·22	$f_2^{1*}p_3^2$
3446·97	1	—	29002·73	$f_1^{1*}p_2^2$	3442·68	2	III.A	29038·87	$f_3^{1*}p_3^2$
3426·99	2	III.A	29171·76	$f_2^{1*}p_2^2$	3401·52	4	III.	29390·18	$f_4^{1*}p_3^2$

Interval ratios, Δf^{1*} as in No. IX.
Δp^2 as in No. II.

Laporte attributes this multiplet to the ($f^{1*}p^2$) combination rather than to (f^{1*}D) in spite of the transition in k, and considers that his arrangement is confirmed by the Zeeman resolution of the lines.

MULTIPLET No. XVII.

Combination $p_i^{\mathrm{I}} - d_i^2 \quad \Delta k = -1.$

6302·51	6	V.	15862·31	$p_1^{\mathrm{I}} d_0^2$	6301·52	15	IV.	15864·79	$p_2^{\mathrm{I}} d_2^2$
6336·84	12	V.	15776·37	$p_1^{\mathrm{I}} d_1^2$	6411·67	12	IV.	15592·24	$p_2^{\mathrm{I}} d_3^2$
6408·04	8	V.	15601·08	$p_1^{\mathrm{I}} d_2^2$	6141·73	4	V.	16277·41	$p_3^{\mathrm{I}} d_2^2$
6232·67	5	V.	16040·06	$p_2^{\mathrm{I}} d_1^2$	6246·34	15	V.	16004·94	$p_3^{\mathrm{I}} d_3^2$
					6400·02	25	III.	15620·63	$p_3^{\mathrm{I}} d_2^4$

Interval ratios, Δp^1 as in No. I.

Δd^2 86·9 : 175·3 : 272·5 : 384·3 = $\begin{cases} 0{\cdot}9 : 1{\cdot}8 : 2{\cdot}8 : 4 \text{ obs.} \\ 1{\cdot}0 : 2{\cdot}0 : 3{\cdot}0 : 4 \text{ calc.} \end{cases}$

MULTIPLET No. XVIII.

Combination $d_i^{\mathrm{I}*} - d_i^2 \quad \Delta k = 0.$

5273·18	1	—	18958·64	$d_0^{\mathrm{I}*} d_1^2$	5339·95	12	V.	18721·57	$d_2^{\mathrm{I}*} d_3^2$
5229·84	5*n*	V.	19115·72	$d_1^{\mathrm{I}*} d_0^2$	5208·61	7	IV.	19193·65	$d_3^{\mathrm{I}*} d_2^2$
5253·48	1	—	19029·71	$d_1^{\mathrm{I}*} d_1^2$	5283·63	18	IV.	18921·12	$d_3^{\mathrm{I}*} d_3^2$
5302·32	10	V.	18854·45	$d_1^{\mathrm{I}*} d_2^2$	5393·19	10	IV.	18536·78	$d_3^{\mathrm{I}*} d_4^2$
5215·20	6	IV.	19169·41	$d_2^{\mathrm{I}*} d_1^2$	5217·41	5	V.	19161·28	$d_4^{\mathrm{I}*} d_3^2$
5263·32	8	V.	18994·15	$d_2^{\mathrm{I}*} d_2^2$	5324·20	30	IV.	18776·96	$d_4^{\mathrm{I}*} d_4^2$

Interval ratios, Δd^{1*} as in No. III.
Δd^2 as in No. XVII.

MULTIPLET No. XIX.

Combination $f_i^{\mathrm{I}} - d_i^2 \quad \Delta k = +1.$

5576·11	10	IV.	17928·69	$f_1^{\mathrm{I}} d_0^2$	5572·86	30	IV.	17939·15	$f_3^{\mathrm{I}} d_2^2$
5602·97	10	IV.	17842·76	$f_1^{\mathrm{I}} d_1^2$	5658·84	10	IV.	17666·58	$f_3^{\mathrm{I}} d_3^2$
5658·54	1	—	17667·50	$f_1^{\mathrm{I}} d_2^2$	5784·69	1	—	17282·23	$f_3^{\mathrm{I}} d_4^2$
5569·63	20	IV.	17949·53	$f_2^{\mathrm{I}} d_1^2$	5586·77	40	IV.	17894·46	$f_4^{\mathrm{I}} d_3^2$
5624·56	10	IV.	17774·23	$f_2^{\mathrm{I}} d_2^2$	5709·40	10	IV.	17510·15	$f_4^{\mathrm{I}} d_4^2$
5712·15	1	—	17501·71	$f_2^{\mathrm{I}} d_3^2$	5615·66	50	IV.	17802·37	$f_5^{\mathrm{I}} d_4^2$

Interval ratios, Δf^1 as in No. VI.
Δd^2 as in No. XVII.

TABLE LXXXI.

Triplet System.

MULTIPLET No. XX.

Combination $F_i^{I*} - D_i^{I*}$ $\Delta k = +1$.

3841·05	80*r*	II.	26027·17	$F_2^{I*}D_1^{I*}$	3966·07	10	III.	25206·77	$F_2^{I*}D_3^{I*}$
3888·52	20	II.	25709·46	$F_2^{I*}D_2^{I*}$	3902·95	20	II.	25614·41	$F_3^{I*}D_3^{I*}$
3827·83	75*r*	II.	26117·10	$F_3^{I*}D_2^{I*}$	3815·84	100*r*	II.	26199·11	$F_4^{I*}D_3^{I*}$

Interval ratios, ΔF^{1*} 407·6 : 584·7 = { 2·8 : 4 obs. / 3·0 : 4 calc.

ΔD^{1*} 317·7 : 502·7 = { 1·9 : 3 obs. / 2·0 : 3 calc.

This is a triplet which is quite analogous to those of the diffuse series of the alkaline earth metals, but the separations are remarkably great. Indeed, the difference 584·70 is the largest in the whole spectrum.

MULTIPLET No. XXI.

Combination $F_i^{I*} - D_i^{2*}$ $\Delta k = +1$.

5270·36	8	II.	18968·75	$F_2^{I*}D_1^{2*}$	5446·92	6	I.	18353·91	$F_2^{I*}D_3^{2*}$
5341·03	5	II.	18717·80	$F_2^{I*}D_2^{2*}$	5328·54	4	II.	18716·66	$F_3^{I*}D_3^{2*}$
5227·19	8	II.	19125·43	$F_3^{I*}D_2^{2*}$	5167·49	8	II.	19346·40	$F_4^{I*}D_3^{2*}$

Interval ratios, ΔF^{1*} as in No. XX.

ΔD^{2*} 250·95 : 363·89 = { 2·0 : 2·9 obs. / 2·0 · 3·0 calc.

MULTIPLET No. XXII.

Combination $F_i^{I*} - F_i^{I}$ $\Delta k = 0$.

4071·75	40	II.	24552·57	$F_2^{I*}F_2^{I}$	3969·26	30	II.	25186·48	$F_4^{I*}F_3^{I}$
4005·25	25	II.	24960·20	$F_3^{I*}F_2^{I}$	4143·87	30	I.	24125·21	$F_3^{I*}F_4^{I}$
4132·06	25	II.	24194·19	$F_2^{I*}F_3^{I}$	4045·82	60*r*	II.	24709·91	$F_4^{I*}F_4^{I}$
4063·60	45	II.	24601·78	$F_3^{I*}F_3^{I}$					

Interval ratios, ΔF^{1*} as in No. XX.

ΔF^{1} 358·4 : 476·6 = { 3·0 : 4 obs. / 3·0 : 4 calc.

MULTIPLET NO XXIII.

Combination $F_i^{I*} - G_i^{I*}$ $\Delta k = -1$.

4325·77	35	II.	23110·76	$F_2^{I*}G_3^{I*}$	4307·91	35	II.	23206·58	$F_3^{I*}G_4^{I*}$
4250·79	25	II.	23518·41	$F_3^{I*}G_3^{I*}$	4202·03	30	I.	23791·33	$F_4^{I*}G_4^{I*}$
4147·68	10	III.	24103·11	$F_4^{I*}G_3^{I*}$	4271·76	35	II.	23402·96	$F_4^{I*}G_5^{I*}$

Interval ratios, ΔF^{1*} as in No. XX.

ΔG^{1*} 311·8 : 388·4 = $\begin{cases} 4·0 : 5 \text{ obs.} \\ 4·0 : 5 \text{ calc.} \end{cases}$

TABLE LXXXII.

Intercombinations.

MULTIPLET NO. XXIV.

Combination $d_i^I - P_i^I$ $\Delta k = +1$.

2969·36	5	II.	33667·44	$d_1^1P_0^1$	3024·04	15*r*	I.A	33058·78	$d_1^1P_2^1$
2994·50	2	I.	33384·84	$d_0^1P_1^1$	3007·28	12*r*	I.	33242·94	$d_2^1P_2^1$
2986·46	3	III.	33474·72	$d_1^1P_1^1$	2981·45	20*r*	I.	33531·00	$d_3^1P_2^1$
2970·11	?	—	33659·02	$d_2^1P_1^1$					

Interval ratios, Δd^1 as in No. I.

ΔP^1 192·72 : 415·9 = $\begin{cases} 0·9 : 2 \text{ obs.} \\ 1·0 : 2 \text{ calc.} \end{cases}$

The line at $\lambda = 2970·11$ was also used in Multiplet No. VII. as $d_1^1 - f_2^2$. The fact that the two components of the two multiplets have the same wave-length makes it impossible to assign any value to the intensity.

MULTIPLET NO. XXV.

Combination $d_i^I - D_i^{I*}$ $\Delta k = 0$.

2629·60	2	III.	38017·28	$d_0^1D_1^{1*}$	2612·79	2	III.	38261·89	$d_3^1D_2^{1*}$
2623·38	2	III.	38107·43	$d_1^1D_1^{1*}$	2667·92	2	III.A	37471·29	$d_2^1D_3^{1*}$
2610·76	1	III.	38291·61	$d_2^1D_1^{1*}$	2647·57	4	III.	37759·26	$d_3^1D_3^{1*}$
2645·43	2	III.A	37789·78	$d_1^1D_2^{1*}$	2618·72	2	III.	38175·22	$d_4^1D_3^{1*}$
2632·60	4	III.A	37973·89	$d_2^1D_2^{1*}$					

Interval ratios, Δd^1 as in No. I.

ΔD^{1*} as in No. XX.

Laporte states in an addendum to his paper that he has found a multiplet of nine lines between λ 3265·06 and λ 3191·07 formed by the combination $d_i^1 - D_i^{2*}$. This new multiplet must be the second

TABLE LXXXII.—*Continued.*

member of the series $d_i^1 - m\mathrm{D}^*$, of which Multiplet No. XXV. is the first member, since the terms provisionally labelled D^{1*} and D^{2*} are 3D* and 4D*.

MULTIPLET NO. XXVI.

Combination $f_i^{1*} - \mathrm{F}_i^1$ $\Delta k = 0$.

3404·30	2	III.A	29366·20	$f_1^{1*}\mathrm{F}_2^1$	3356·33	1	IV.A	29785·88	$f_4^{1*}\mathrm{F}_3^1$
Calc.	—	—	29535·20	$f_2^{1*}\mathrm{F}_2^1$	3452·28	4	III.	28958·11	$f_3^{1*}\mathrm{F}_4^1$
3355·52	1	—	29793·13	$f_3^{1*}\mathrm{F}_2^1$	3410·91	1	—	29309·36	$f_4^{1*}\mathrm{F}_4^1$
3426·39	4	III.A	29176·87	$f_2^{1*}\mathrm{F}_3^1$	3359·50	3	III.A	29757·84	$f_5^{1*}\mathrm{F}_4^1$
3396·39	1	—	29434·64	$f_3^{1*}\mathrm{F}_3^1$					

Interval ratios, Δf^{1*} as in No. IX.
$\Delta \mathrm{F}^1$ as in No. XXII.

The intensities as given by Burns contravene the intensity rule, but this may be due to the fact that they are very small. The differences are the same as previously found, and thus confidence may be placed in the above structure in spite of the intensities.

MULTIPLET NO. XXVII.

Combination $f_i^{1*} - \mathrm{G}_i^{1*}$ $\Delta k = -1$.

3558·52	30	II.	28093·55	$f_2^{1*}\mathrm{G}_3^{1*}$	3521·26	15	II.	28390·79	$f_4^{1*}\mathrm{G}_4^{1*}$
3526·17	15	II.	28351·32	$f_3^{1*}\mathrm{G}_3^{1*}$	3466·50	3	III.A	28839·29	$f_5^{1*}\mathrm{G}_4^{1*}$
3483·01	3	III.A	28702·58	$f_4^{1*}\mathrm{G}_3^{1*}$	3570·10	100R	I.	28002·43	$f_4^{1*}\mathrm{G}_5^{1*}$
3565·38	60*r*	I.	28039·50	$f_3^{1*}\mathrm{G}_4^{1*}$	3513·82	30	II.	28450·93	$f_5^{1*}\mathrm{G}_5^{1*}$

Interval ratios, Δf^{1*} as in No. IX.
$\Delta \mathrm{G}^{1*}$ as in No. XXIII.

MULTIPLET NO. XXVIII.

Combination $f_i^{1*} - \mathrm{P}_i^1$ $\Delta k = +2$.

3786·68	8	III.	26400·90	$f_1^{1*}\mathrm{P}_0^1$	3876·04	15	III.	25792·20	$f_1^{1*}\mathrm{P}_2^1$
3814·53	10	III.A	26208·17	$f_1^{1*}\mathrm{P}_1^1$	3850·82	15*r*	II.	25961·16	$f_2^{1*}\mathrm{P}_2^1$
3790·09	10	II.	26377·11	$f_2^{1*}\mathrm{P}_1^1$	3812·97	25R	II.	26218·89	$f_3^{1*}\mathrm{P}_2^1$

Interval ratios, Δf^{1*} as in No. IX.
$\Delta \mathrm{P}^1$ as in No. XXIV.

MULTIPLET NO. XXIX.

Combination $F_i^{1*} - d_i^{3*}$ $\Delta k = +1$.

3643·72	1	IV.	27436·6	$F_2^{1*}d_1^{3*}$	3647·43	3	IV.	27408·8	$F_3^{1*}d_3^{3*}$
3666·92	1	—	27263·1	$F_2^{1*}d_2^{3*}$	3571·23	4	IV.A	27993·60	$F_4^{1*}d_3^{3*}$
3612·94	4	IV.A	27670·5	$F_3^{1*}d_2^{3*}$	Calc.	—	—	27064·8	$F_3^{1*}d_4^{3*}$
3702·49	1	IV.A	27001·2	$F_2^{1*}d_3^{3*}$	3615·66	1	—	27649·6	$F_4^{1*}d_4^{3*}$

Interval ratios, ΔF^{1*} as in No. XX.
Δd^{3*} as in No. V.

MULTIPLET NO. XXX.

Combination $F_i^{1*} - f_i^2$ $\Delta k = 0$.

4602·01	2	—	21723·57	$F_2^{1*}f_1^2$	Calc.	—	—	22352·5	$F_4^{1*}f_3^2$
4632·92	3	III.	21578·63	$F_2^{1*}f_2^2$	4654·50	4	II.	21478·58	$F_3^{1*}f_4^2$
4547·03	2	—	21986·24	$F_3^{1*}f_2^2$	4531·16	5	I.	22063·26	$F_4^{1*}f_4^2$
4680·30	2	—	21360·18	$F_2^{1*}f_3^2$	4602·95	4	I.	21719·15	$F_4^{1*}f_5^2$
4592·66	4	I.	21767·80	$F_3^{1*}f_3^2$					

Interval ratios, ΔF^{1*} as in No. XX.
Δf^2 as in No. VII.

MULTIPLET NO. XXXI.

Combination $F_i^{1*} - g_i^{1*}$ $\Delta k = -1$.

4367·91	2	III.A	22887·83	$F_2^{1*}g_2^{1*}$	4229·75	1	III.	23635·39	$F_4^{1*}g_3^{1*}$
4291·47	4	I.A	23295·48	$F_3^{1*}g_2^{1*}$	4404·75	30	II.	22696·40	$F_3^{1*}g_4^{1*}$
4415·13	20	II.	22643·06	$F_2^{1*}g_3^{1*}$	4294·13	15	II.	23281·05	$F_4^{1*}g_4^{1*}$
4337·05	10	II.	23050·64	$F_3^{1*}g_3^{1*}$	4383·55	45r	II.	22806·18	$F_4^{1*}g_5^{1*}$

Interval ratios, ΔF^{1*} as in No. XX.
Δg^{1*} as in No. XV.

Laporte found two multiplets which he allocated to a septet system for reasons which will be given below. These two multiplets contained thirteen and nine lines respectively, and their structure is given in Table LXXXIII.

TABLE LXXXIII.

SEPTET SYSTEM.

MULTIPLET NO. XXXII.

Combination $\delta_i - \delta_i^*$ $\Delta k = 0$.

4210·36	6	III.	23744·22	$\delta_1\delta_1^*$	4187·81	6	III.	23872·16	$\delta_3\delta_4^*$
4191·45	6	III.	23851·38	$\delta_1\delta_2^*$	4271·17	7	III.	23406·22	$\delta_4\delta_3^*$
4233·61	6	III.	23613·86	$\delta_2\delta_1^*$	4235·95	8	III.	23600·83	$\delta_4\delta_4^*$
Calc.	—	—	23720·97	$\delta_2\delta_2^*$	4198·31	6	III.	23812·41	$\delta_4\delta_5^*$
4187·05	6	III.	23876·49	$\delta_2\delta_3^*$	4299·25	7	III.	23253·32	$\delta_5\delta_4^*$
4250·13	7	III.	23522·11	$\delta_3\delta_2^*$	4260·49	10	III.	23464·87	$\delta_5\delta_5^*$
4222·23	5	III.	23677·50	$\delta_3\delta_3^*$					

Interval ratios, $\Delta\delta^*$ 107·1 : 155·5 : 194·7 : 211·6 = { 2·3 : 3·2 : 4·0 : 4·3 obs. / 2·0 : 3·0 : 4·0 : 5·0 calc.

$\Delta\delta$ 130·4 : 198·9 : 271·3 : 347·5 = { 1·9 : 3·0 : 4·0 : 5·2 obs. / 2·0 : 3·0 : 4·0 : 5·0 calc.

MULTIPLET NO. XXXIII.

Combination $\pi_i - \delta_i$ $\Delta k = -1$.

5191·48	7	IV.	19257·03	$\pi_2\delta_1$	5068·78	4	V.	19723·16	$\pi_4\delta_3$
5266·98	5	IV.	19126·60	$\pi_2\delta_2$	5266·57	8	IV.	18982·43	$\pi_3\delta_4$
5139·27	6	IV.	19452·68	$\pi_3\delta_2$	5139·48	8	IV.	19451·84	$\pi_4\delta_4$
5281·80	5	IV.	18927·71	$\pi_2\delta_3$	5232·95	8	III.	19104·39	$\pi_4\delta_5$
5192·36	8	IV.	19253·73	$\pi_3\delta_3$					

Interval ratios, $\Delta\delta$ as in No. XXXII.

$\Delta\pi$ 326·06 : 469·42 = { 2·9 : 4·2 obs. / 3·0 : 4·0 calc.

The arguments in favour of attributing these two multiplets to a septet system are as follows: In the first place, the second multiplet is obviously due to the combination of a triplet and a quintet term, and consequently if we keep within the limits set by the selection principle for the azimuthal quantum number, the combination is doubtless of the (*pd*) type. Such combinations may belong to the quintet or a septet system. In the second place, the first multiplet of thirteen lines must be due to the combination of two five-fold terms, that is to say $\Delta k = 0$ and consequently the combination must be of the type (*dd**), since the *d*-term is common to both multiplets. Now if the *d*- and *d**-terms belonged to the quintet system, their inner quantum numbers would be 0, 1, 2, 3, 4 and the line $\lambda = 4210{\cdot}36$ would be due to the transition $i \rightarrow i - 0 \rightarrow 0$, which as we know is expressly forbidden. If we attribute the five-fold *d*-terms to a septet system then we have $i = 1, 2, 3, 4, 5$ and the line $\lambda = 4210{\cdot}36$ is due to the

transition $i \rightarrow i = 1 \rightarrow 1$. This is further supported by the interval ratios, which in the case of the δ- and π-terms agree very well with calculated values.

It is evident from the foregoing list of multiplets that the most frequent and also the strongest combinations involve the terms d^1 and f^1, whilst the combinations involving the term d^2 give weak lines which belong to higher temperature classes. It may further be seen that in every case the magnitude of the terms increases with the inner quantum number, that is to say,

$$p_3 > p_2 > p_1$$

and

$$d_4 > d_3 > d_2 > d_1 > d_0, \text{ etc.}$$

All the terms are therefore reversed terms, and though at first sight this may appear somewhat startling, it is to be expected from the cases of vanadium, chromium, and manganese. Thus vanadium exhibits no reversed term, chromium exhibits two reversed terms only, and in the case of manganese about half of the recognised terms are reversed. It is not surprising therefore that in iron we find only reversed terms.

Now, the absorption spectrum of iron vapour has been examined by Fraülein Gieseler and Dr. Grotrian [1] who found that at temperatures of 1230° to 1250° the following appear as absorption lines, λ — 3886·29, 3859·91, 3745·56, 3737·14, 3719·94, 3047·61, 3021·08, 3020·64,[2] 2973·24, 2966·90, and 2719·04. Of these lines the most intense was λ — 3859·91 and the lines λ — 3047·6 and 2719·04 were less certain than the remainder.

From the tables of the multiplets given above it will be seen that these lines are due to the combinations shown in Table LXXXIV.

TABLE LXXXIV.

3886·29	$d^{\mathrm{I}}_3 - d^{\mathrm{I}*}_3$	40R
3859·91	$d^{\mathrm{I}}_4 - d^{\mathrm{I}*}_4$	300R
3745·56	$d^{\mathrm{I}}_2 - f^{\mathrm{I}}_3$	150R
3737·14	$d^{\mathrm{I}}_3 - f^{\mathrm{I}}_4$	200R
3719·94	$d^{\mathrm{I}}_4 - f^{\mathrm{I}}_5$	300R
3047·61	$d^{\mathrm{I}}_2 - d^{2*}_2$	100R
3021·08	$d^{\mathrm{I}}_3 - d^{2*}_3$	150R
3020·64	$d^{\mathrm{I}}_4 - d^{2*}_4$	200R
2973·24	$d^{\mathrm{I}}_3 - f^{2}_4$	60R
2966·90	$d^{\mathrm{I}}_4 - f^{2}_5$	125R
2719·04	$d^{\mathrm{I}}_4 - p^{2}_3$	60R

[1] *Zeitsch. für Phys.*, **22**, 245 (1924); see also E. v. Angerer and G. Joos, *Naturwissenschaften*, **12**, 140 (1924).

[2] This line was not resolved.

In every case the final level is the five-fold d^1-term and the strongest lines are given by transitions to the d_4^1 or lowest level. This d^1-term must therefore be the fundamental level of the iron atom, and this means that the twenty-sixth electron must be bound in a 3_3-orbit.

Two points may be noted here, namely, the absence of a sharp term in the three systems, and also the appearance, as in vanadium, of terms with an azimuthal quantum number 5. In a footnote to his paper Laporte gives a triplet which can be attributed to a combination $s_2 - p_i$ shown in Table LXXXV.

TABLE LXXXV.

	p				
i	3		2		1
	12 III.		10 III.		9 III.
	4282·41		4315·09		4352·74
$s2$	23344·80	176·81	23167·99	200·39	22967·60

$$\Delta k = -1.$$

Order of intensities, $s_2 - p_3$ 12
$s_2 - p_2$ 10
$s_2 - p_1$ 9

The interval ratios are quite abnormal as in the case of the d-term of mercury. This same p-term recurs in a combination (pp^*) between $\lambda = 4030{\cdot}19$ and $\lambda = 3943{\cdot}35$. The s-term cannot be considered as the fundamental term since the above three lines belong to the temperature class III.

When we consider the asterisk and non-asterisk terms it would seem that the following combinations occur:—

and that no combinations occur of the type (pd^*), (df^*), or (d^*f). From this we may formulate the following extension of the selection principle for transitions in the azimuthal quantum number k: In combinations between asterisk and non-asterisk terms, only those transitions are possible in which $\Delta k = 0$, and in combinations between two asterisk or between two non-asterisk terms only those transitions are possible in which $\Delta k = \pm 1$. Laporte illustrates this law by Fig. 22, where the possible transitions are indicated by the horizontal and vertical arrows, those indicated by the oblique dotted arrows being forbidden.

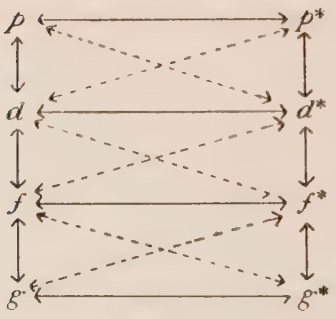


FIG. 22.

As was previously stated it has not been found possible to determine the absolute magnitude of the terms, but Laporte estimates that the largest term d^1 has the value

$$d^1 = 48000,$$

and in his first paper he gives the differences between this term and all the other terms of the quintet and triplet systems.

Soon after the publication of this first paper by Laporte a further communication was published by Walters,[1] which gave details of many new multiplets together with their term relationships. In his second paper Laporte [2] begins by confirming his allocation of the two multiplets Nos. XXXII. and XXXIII. to a septet system from the Zeeman patterns given by the lines. He then assigns to the septet system a third multiplet which was discovered by Walters. The detailed structure of this multiplet is given in Table LXXXVI.

TABLE LXXXVI.

MULTIPLET NO. XXXIV.

Combination $\phi_i - \delta_i$ $\quad \Delta k = +1$.

4878·23	12	III.	20493·53	$\phi_0\delta_1$	4985·56	7	V.	20052·34	$\phi_3\delta_4$
4872·15	20	III.	20519·08	$\phi_1\delta_1$	4891·51	50	III.	20437·90	$\phi_4\delta_3$
4903·33	12	III.	20388·65	$\phi_1\delta_2$	4957·31	20	III.	20166·60	$\phi_4\delta_4$
4859·76	15	III.	20571·49	$\phi_2\delta_1$	5044·22	1	—	19819·09	$\phi_4\delta_5$
4890·77	25	III.	20440·99	$\phi_2\delta_2$	4920·52	60	III.	20317·40	$\phi_5\delta_4$
4938·83	10	IV.	20242·08	$\phi_2\delta_3$	5006·13	20	III.	19969·94	$\phi_5\delta_5$
4871·33	25	III.	20522·54	$\phi_3\delta_2$	4957·61	60	III.	20165·38	$\phi_6\delta_5$
4919·01	30	III.	20323·64	$\phi_3\delta_3$					

Interval ratios, $\Delta\delta$ as in No. XXXII.

$\Delta\phi$ 25·6 : 52·4 : 81·6 : 114·3 : 150·8 : 195·4 = $\begin{cases} 0{\cdot}8 : 1{\cdot}6 : 2{\cdot}5 : 3{\cdot}5 : 4{\cdot}6 : 6{\cdot}0 \text{ obs.} \\ 1{\cdot}0 : 2{\cdot}0 : 3{\cdot}0 : 4{\cdot}0 : 5{\cdot}0 : 6{\cdot}0 \text{ calc.} \end{cases}$

As was pointed out by Walters the values of $\Delta\phi$ are distinctly smaller than in all the other iron terms. Probably we see here the decrease in $\Delta\nu$ with increase in the azimuthal quantum number, which up to the present has not been noticeable in the case of iron.

These three multiplets clearly establish the existence of the septet system with four terms π, δ^*, ϕ, δ, and the question arises as to how these are to be fitted in the scheme of levels of the quintet and triplet terms. Three of them, namely, ϕ, δ^*, and π, form combinations with the fundamental d^1 term of the quintet system, which are set forth in Table LXXXVII.

[1] *J. Opt. Soc.*, America, **8**, 245 (1924).
[2] *Zeitsch. für Phys.*, **26**, 1 (1924).

TABLE LXXXVII.

MULTIPLET NO. XXXV.

Combination $d_i^{\mathrm{I}} - \phi_i \quad \Delta k = -1.$

4466·56	12	I.	22382·35	$d_1^{\mathrm{I}}\phi_0$	4461·66	12	I.	22406·92	$d_2^{\mathrm{I}}\phi_3$
4489·74	12	I.A	22266·76	$d_0^{\mathrm{I}}\phi_1$	Calc.	—	—	22695·00	$d_3^{\mathrm{I}}\phi_3$
Calc.	—	—	22356·71	$d_1^{\mathrm{I}}\phi_1$	Calc.	—	—	23110·92	$d_4^{\mathrm{I}}\phi_3$
4435·15	10	I.A	22540·82	$d_2^{\mathrm{I}}\phi_1$	4427·31	12	I.	22580·74	$d_3^{\mathrm{I}}\phi_4$
4482·18	4	I.A	22304·36	$d_1^{\mathrm{I}}\phi_2$	4347·24	1	I.A	22996·66	$d_4^{\mathrm{I}}\phi_4$
4445·48	1	—	22488·47	$d_2^{\mathrm{I}}\phi_2$	4375·93	15	I.	22845·87	$d_4^{\mathrm{I}}\phi_5$
4389·25	10	I.A	22776·55	$d_3^{\mathrm{I}}\phi_2$					

MULTIPLET NO. XXXVI.

Combination $d_i^{\mathrm{I}} - \delta_i^* \quad \Delta k = 0.$

5250·21	1	I.A	19041·55	$d_0^{\mathrm{I}}\delta_1^*$	5247·05	2	I.A	19053·02	$d_2^{\mathrm{I}}\delta_3^*$
5225·53	2	I.A	19131·48	$d_1^{\mathrm{I}}\delta_1^*$	5168·90	3	I.A	19341·08	$d_3^{\mathrm{I}}\delta_3^*$
Calc.	—	—	19315·64	$d_2^{\mathrm{I}}\delta_1^*$	5060·09	1	—	19755·98	$d_4^{\mathrm{I}}\delta_3^*$
5254·96	2	I.A	19024·37	$d_1^{\mathrm{I}}\delta_2^*$	Calc.	—	—	19146·50	$d_3^{\mathrm{I}}\delta_4^*$
5204·59	2	I.A	19208·49	$d_2^{\mathrm{I}}\delta_2^*$	5110·41	4	I.	19562·45	$d_4^{\mathrm{I}}\delta_4^*$
Calc.	—	—	19496·54	$d_3^{\mathrm{I}}\delta_2^*$	5166·29	3	I.A	19350·88	$d_4^{\mathrm{I}}\delta_5^*$

The structure of this multiplet is similar to that of the *df* combination of the quintet system, the only difference being found in the distribution of the intensities (see Nos. VI., VII., and VIII.).

MULTIPLET NO. XXXVII.

Combination $d_i^{\mathrm{I}} - \pi_i \quad \Delta k = +1.$

4232·72	8	I.A	23618·82	$d_1^{\mathrm{I}}\pi_2$	4206·70	12	I.A	23764·91	$d_3^{\mathrm{I}}\pi_3$
4199·99	9	I.A	23802·89	$d_2^{\mathrm{I}}\pi_2$	4134·34	1	—	24180·84	$d_4^{\mathrm{I}}\pi_3$
Calc.	—	—	24090·95	$d_3^{\mathrm{I}}\pi_2$	4291·47	10	I.A	23295·50	$d_3^{\mathrm{I}}\pi_4$
4258·32	10	I.A	23476·85	$d_2^{\mathrm{I}}\pi_3$	4216·19	10	I.	23711·47	$d_4^{\mathrm{I}}\pi_4$

It is interesting to note that all the lines of these last three multiplets belong to the temperature class I.

In order to determine the relationship between the three systems, triplet, quintet, and septet, we calculate the wave-lengths of the lines given by the combinations $F_i^{\mathrm{I}*} - \phi_i$ and $F_i^{\mathrm{I}*} - \delta_i^*$, when it is seen that none of them appear in the spectrum, that is to say, combinations between triplet and septet terms do not occur. The three septet terms ϕ, π, and δ^* thus lie above the fundamental d^1-term,

but below the quintet d^*-term. It follows therefore that the most easily excited line will be

$$d_4^{\mathrm{I}} - \delta_5^* = 19350{\cdot}88, \quad \lambda = 5166{\cdot}29,$$

and not $$d_4^{\mathrm{I}} - d_4^{\mathrm{I}*} = 25900{\cdot}00, \quad \lambda = 3859{\cdot}91,$$

as was stated in the earlier paper. For the same reason the line

$$d_4^{\mathrm{I}} - \phi_5 = 22845{\cdot}87, \quad \lambda = 4375{\cdot}93,$$

will precede in order of excitation the $d_4^{\mathrm{I}} - d_4^{\mathrm{I}*}$ line, and this agrees with King's observation that this line at 1400° is the most intense line. Further, the other lines at longer wave-lengths than $\lambda = 4000$, which are visible in the electric furnace spectrum at 1400°, belong to the quintet-septet combinations

4216·12	(2)	$d_4^{\mathrm{I}} - \pi_4$
4427·31	(8)	$d_3^{\mathrm{I}} - \phi_4$
4461·66	(4)	$d_2^{\mathrm{I}} - \phi_3$
8442·18	(2)	$d_1^{\mathrm{I}} - \phi_2$

The small intensity of these lines in the arc spectrum compared with that of the $d_4^{\mathrm{I}} - d_4^{\mathrm{I}*}$ line ($\lambda = 3860$) is remarkable. This may be explained by the assumption that in the combination of quintet and septet terms the probability of transition is smaller than in the combinations of two quintet terms or of a quintet and triplet term.

Mention was made on p. 202 of a combination of an abnormal p-term with a sharp term. The intervals of this p-term are 200·39 and 176·81, and in his later paper Walters records multiplets with these intervals, but doubts the correctness of the arrangement on account of the anomalous intervals. Laporte, however, is convinced that the term is a true p-term which contravenes the interval rule. He gives several multiplets, also noted by Walters, in which this term takes part. In the first of these the combination occurs with the p^2-term which took part in multiplets Nos. II. and XVI. and consequently it must be a p^*-term, in obedience to the selection principle stated on p. 202. In the multiplets given in Table LXXVIII. the allocation of the lines is confirmed by their Zeeman patterns.

TABLE LXXXVIII.

MULTIPLET No. XXXVIII.

Combination $p_i^* - p_i^2 \quad \Delta k = 0.$

5131·48	1	—	19482·16	$p_1^* p_1^2$	5098·71	8	IV.	19607·36	$p_2^* p_2^2$
5079·23	6	IV.	19682·54	$p_2^* p_1^2$	5250·65	6	IV.	19039·97	$p_2^* p_3^2$
5198·72	4	IV.	19230·16	$p_1^* p_2^2$	5202·34	8	IV.	19216·76	$p_3^* p_3^2$
5142·54	1	—	19430·55	$p_2^* p_2^2$					

TABLE LXXXVIII.—*Continued.*

MULTIPLET No. XXXIX.

Combination $p_i^* - s_i^{2*}$ $\Delta k = +1$.

4352·74	9	III.	22967·60	$p_1^* s_2^{2*}$	4282·41	12	III.	23344·80	$p_3^* s_2^{2*}$
4315·09	10	III.	23167·99	$p_2^* s_2^{2*}$					

MULTIPLET No. XL.

Combination $p_i^* - p_i^3$ $\Delta k = 0$.

3974·77	1	—	25151·61	$p_1^* p_1^3$	3949·96	4	III.	25309·60	$p_3^* p_2^3$
3943·35	1	IV.	25352·02	$p_2^* p_1^3$	4030·19	3*n*	IV.	24805·71	$p_2^* p_3^3$
4009·72	5	III.	24932·39	$p_1^* p_2^3$	4001·67	3	III.	24982·55	$p_3^* p_3^3$
3977·75	5	III.	25132·78	$p_2^* p_2^3$					

Interval ratio, Δp^3 219·23 : 327·06 = $\begin{cases} 2{\cdot}0 : 3{\cdot}0 \text{ obs.} \\ 2{\cdot}0 : 3{\cdot}0 \text{ calc.} \end{cases}$

This is a new p-term and just as was the case with the p^2-term (No. XVI.) it combines with the f^{1*}-term in contradiction of the selection principle of the azimuthal quantum number to give the multiplet in Table LXXXIX.

TABLE LXXXIX.

MULTIPLET No. XLI.

Combination $f_i^{1*} - p_i^3$ $\Delta k = +2$.

2862·50	4	IV.	34924·31	$f_1^{1*} p_1^3$	2845·60	8	III.	35131·71	$f_3^{1*} p_2^3$
2848·71	5	III.	35093·27	$f_2^{1*} p_1^3$	2893·76	1	IV.A	34546·98	$f_2^{1*} p_3^3$
2880·58	2	IV.	34705·11	$f_1^{1*} p_2^3$	2872·34	7	III.	34804·65	$f_3^{1*} p_3^3$
2866·63	7	II.	34873·97	$f_2^{1*} p_2^3$	2843·63	10	III.	35156·02	$f_4^{1*} p_3^3$

There also appears to exist a multiplet at $\lambda = 2389{\cdot}98$ to $\lambda = 2350{\cdot}43$ due to the combination of the p^3-term with the fundamental d^1-term. There also exist in the region near to $\lambda = 3300$ numerous combinations between the p^*-term and unknown term levels. Laporte does not give details of the latter, since the lines are weak and do not belong to any special temperature class. He gives with reserve two multiplets in which the p^*-term combines with two other terms. These are given in Table XC. and the first is the more certain, since the Zeeman pattern of one line ($\lambda = 3286{\cdot}76$) shows that the combination is of the $p^* p$ type.

TABLE XC.

MULTIPLET No. XLII.

Combination $p_i^* - p_i^4 \quad \Delta k = 0.$

3292·60	8	IV.	30362·43	$p_1^* p_1^4$	3265·62	15	III.	30613·24	$p_3^* p_2^4$
3271·01	15	III.	30562·79	$p_2^* p_1^4$	3305·98	20	III.	30239·55	$p_2^* p_3^4$
3306·36	20	III.	30236·08	$p_1^* p_2^4$	3286·76	20	III.	30416·34	$p_3^* p_3^4$
3284·59	5	IV.	30436·43	$p_2^* p_2^4$					

Interval ratio, Δp^4 126·36 : 196·89 = $\begin{cases} 1{\cdot}9 : 3{\cdot}0 \text{ obs.} \\ 2{\cdot}0 : 3{\cdot}0 \text{ calc.} \end{cases}$

MULTIPLET No. XLIII.

Combination $p_i^* - Z_i$.

3406·81	6	IV.	29344·63	$p_1^* Z_1$	3372·08	3	IV.	29646·79	$p_3^* Z_2$
3383·70	5	IV.	29545·02	$p_2^* Z_1$	3404·35	6	IV.	29365·78	$p_2^* Z_3$
3415·54	4	IV.	29269·61	$p_1^* Z_2$	3383·99	8	IV.	29542·49	$p_3^* Z_2$
3392·31	8	IV.	29470·03	$p_2^* Z_2$					

Interval ratio, ΔZ 75·01 : 104·28 = $\begin{cases} 2{\cdot}2 : 3{\cdot}0 \text{ obs.} \\ 2{\cdot}0 : 3{\cdot}0 \text{ calc.} \end{cases}$

It is probable that the Z-term is a D* triplet term, since it combines with the F^{1*} term to give the multiplet shown in Table XCI.

TABLE XCI.

MULTIPLET No. XLIV.

Combination $F_i^{1*} - Z_i$.

2914·31	3	IV.	34303·48	$F_2^{1*} Z_1$	2929·62	2	IV.	34124·18	$F_2^{1*} Z_3$
2920·69	5	IV.	34228·45	$F_2^{1*} Z_2$	2895·04	8	III.	34531·79	$F_3^{1*} Z_3$
2886·32	3	IV.	34636·09	$F_3^{1*} Z_2$	2846·83	3	IV.	35116·49	$F_4^{1*} Z_3$

Walters found evidence of a term which he named U and which is analogous to Laporte's d^2-term. According to Walters the U-term is four-fold, which cannot be the case in a system of uneven multiplicities. Laporte interpretes it as an f^{2*}-term and gives three multiplets formed by combination of this term with the f^1-, d^{1*}-, and g^{1*}-terms. These are set forth in Table XCII.

TABLE XCII.

Multiplet No. XLV.

Combination $f^{1}_{i} - f^{2*}_{i}$ $\Delta k = 0$.

4863·66	2	—	20554·94	$f^{1}_{1}f^{2*}_{1}$	5002·82	2	—	19983·19	$f^{1}_{3}f^{2*}_{4}$
4907·75	1	—	20370·27	$f^{1}_{1}f^{2*}_{2}$	4855·69	2	—	20588·66	$f^{1}_{4}f^{2*}_{3}$
4838·52	2	—	20661·72	$f^{1}_{2}f^{2*}_{1}$	4946·40	2	IV.	20211·09	$f^{1}_{4}f^{2*}_{4}$
4882·17	2	—	20477·01	$f^{1}_{2}f^{2*}_{2}$	5039·27	2	—	19838·64	$f^{1}_{4}f^{2*}_{5}$
4950·12	1	—	20195·91	$f^{1}_{2}f^{2*}_{3}$	Calc.	—	—	20503·37	$f^{1}_{5}f^{2*}_{4}$
4843·16	2	—	20641·96	$f^{1}_{3}f^{2*}_{2}$	4966·10	5	V.	20130·91	$f^{1}_{5}f^{2*}_{5}$
4910·03	2	—	20360·81	$f^{1}_{3}f^{2*}_{3}$					

Interval ratio, Δf^{2*} 184·7 : 281·1 : 377·6 : 372·5 = $\begin{cases} 1{\cdot}95 : 3{\cdot}0 : 4{\cdot}0 : 3{\cdot}95 \text{ obs.} \\ 2{\cdot}0 : 3{\cdot}0 : 4{\cdot}0 : 5{\cdot}0 \text{ calc.} \end{cases}$

As can be seen the interval rule is broken, but the distribution of intensities and the Zeeman pattern of the line at $\lambda = 4966{\cdot}10$ justify the inclusion of the f^{2*}-term. Especially is it noteworthy that the same term is found in the two following multiplets :—

Multiplet No. XLVI.

Combination $d^{1*}_{i} - f^{2*}_{i}$ $\Delta k = -1$.

4613·22	2*n*	V.	21670·79	$d^{1*}_{0}f^{2*}_{1}$	4565·68	1	—	21896·41	$d^{1*}_{3}f^{2*}_{2}$
4598·14	1	—	21741·87	$d^{1*}_{1}f^{2*}_{1}$	4625·06	3	IV.	21615·29	$d^{1*}_{3}f^{2*}_{3}$
4637·52	3	IV.	21557·22	$d^{1*}_{1}f^{2*}_{2}$	4707·29	8	IV.	21237·72	$d^{1*}_{3}f^{2*}_{4}$
4568·79	1	—	21881·52	$d^{1*}_{2}f^{2*}_{1}$	Calc.	—	—	21855·51	$d^{1*}_{4}f^{2*}_{3}$
4607·67	3*n*	V.	21696·90	$d^{1*}_{2}f^{2*}_{2}$	4654·64	5	IV.	21477·94	$d^{1*}_{4}f^{2*}_{4}$
4668·15	6	IV.	21415·76	$d^{1*}_{2}f^{2*}_{3}$	4736·79	12	II.?	21105·47	$d^{1*}_{4}f^{2*}_{5}$

Multiplet No. XLVII.

Combination $g^{1*}_{i} - f^{2*}_{i}$ $\Delta k = +1$.

8085·2	5	—	12364·9	$g^{1*}_{2}f^{2*}_{1}$	7999·0	6	—	12498·1	$g^{1*}_{4}f^{2*}_{3}$
8207·8	1	—	12180·4	$g^{1*}_{2}f^{2*}_{2}$	8248·1	3	—	12120·7	$g^{1*}_{4}f^{2*}_{4}$
8401·4	1	—	11899·5	$g^{1*}_{2}f^{2*}_{3}$	Calc.			11748·2	$g^{1*}_{4}f^{2*}_{5}$
8046·1	5	—	12425·0	$g^{1*}_{3}f^{2*}_{2}$	7937·2	9	—	12595·4	$g^{1*}_{5}f^{2*}_{4}$
8232·3	2	—	12143·9	$g^{1*}_{3}f^{2*}_{3}$	8179·0	1		12223·0	$g^{1*}_{5}f^{2*}_{5}$
8497·0	2		11765·6	$g^{1*}_{3}f^{2*}_{4}$	8220·4	7		12161·5	$g^{1*}_{6}f^{2*}_{5}$

The remarkable divergence of the interval g^{I*}_{56} from the interval rule previously noted in No. XV. is again found here. This means that the g^{I*}_i-levels lie in the following order :—

$$g^{I*}_2 < g^{I*}_3 < g^{I*}_4 < g^{I*}_6 < g^{I*}_5.$$

This may possibly be due to a tendency of this term to change from a reversed term to a normal term, but no other instances of this have as yet been found.

Laporte gives four other multiplets formed by the combination of the f^{2*}-term with the f^2-, d^{2*}-, G^{1*}-terms and with another term, which is possibly a g^*-term, but these need not be detailed.

Walters finds a three-fold term with $i = 2, 3, 4$, which is therefore in all probability a triplet F-term. This combines with the F^{1*}-term to give the multiplet shown in Table XCIII.

TABLE XCIII.

MULTIPLET No. XLVIII.

Combination $F^{I}_i* - F^{o}_i$ $\Delta k = 0$.

5216·28	10	II.	19165·43	$F^{I}_2*F^{o}_2$	5041·76	10	III.	19828·82	$F^{I}_4*F^{o}_3$
5107·65	8	II.	19573·05	$F^{I}_3*F^{o}_2$	5332·91	4	I.	18746·32	$F^{I}_3*F^{o}_4$
5307·36	2	III.	18836·53	$F^{I}_2*F^{o}_3$	5171·60	20	II.	19331·01	$F^{I}_4*F^{o}_4$
5194·95	10	I.	19244·14	$F^{I}_3*F^{o}_3$					

Interval ratio, ΔF^{o} 328·9 : 497·8 = $\begin{cases} 2·65 : 4·0 \text{ obs.} \\ 3·0 : 4·0 \text{ calc.} \end{cases}$

Finally Laporte gives two multiplets due to the combination of a new D*-term with the F^{1*} and d^1-terms. These are set forth in Table XCIV.

TABLE XCIV.

MULTIPLET No. XLIX.

Combination $F^{I}_i* - D^{o}_i*$ $\Delta k = +1$.

5270·36	30	II.	18968·78	$F^{I}_2*D^{o}_1*$	5446·92	40	I.	18353·90	$F^{I}_2*D^{o}_3*$
5341·03	20	II.	18717·78	$F^{I}_2*D^{o}_2*$	5328·54	15	II.	18761·67	$F^{I}_3*D^{o}_3*$
5227·19	40	II.	19125·44	$F^{I}_3*D^{o}_2*$	5167·49	40	II.	19346·37	$F^{I}_4*D^{o}_3*$

The line $\lambda = 5446·92$ also occurs in Multiplet No. IX. and consequently the lines due to the transitions $f^{I*}_2 - d^{I*}_2$ and $F^{I*}_2 - D^{o*}_3$ have almost exactly the same wave-length.

Interval ratio, ΔD^{o*} 251·0 : 363·8 = $\begin{cases} 2·1 : 3·0 \text{ obs.} \\ 2·0 : 3·0 \text{ calc.} \end{cases}$

TABLE XCIV.—*Continued.*

MULTIPLET NO. L.

Combination $d_i^1 - D_i^{0*}$ $\Delta k = 0$.

3229·13	8	II.A	30959·20	$d_0^1D_1^{0*}$	3197·00	1	—	31270·32	$d_3^1D_2^{0*}$
Calc.	—	—	31049·16	$d_1^1D_1^{0*}$	3265·06	15r	I.A	30618·54	$d_2^1D_3^{0*}$
3200·79	6	III.A	31233·29	$d_2^1D_1^{0*}$	3234·62	15r	I.A	30906·62	$d_3^1D_3^{0*}$
3246·02	12	I.	30798·15	$d_1^1D_2^{0*}$	3191·67	15r	I.A	31322·57	$d_4^1D_3^{0*}$
3226·73	5	III.A	30982·25	$d_2^1D_2^{0*}$					

One of the most interesting facts brought out in this second paper by Laporte is the existence of the p^*-term, the interval ratio of which contravenes the Landé rule. In the first paper an extension of the selection principle was brought forward as to the azimuthal quantum number. This states that in combination between asterisk and non-asterisk terms it is necessary that $\Delta k = 0$. It was only possible to establish this by relatively few combinations, but the new p^*-term allows the rule to be tested more rigorously. Laporte calculates the wave-length of the $d_i^1 - p_i^*$ multiplet, where $\Delta k = +1$, and obtains the values set forth in Table XCV.

TABLE XCV.

d^1.

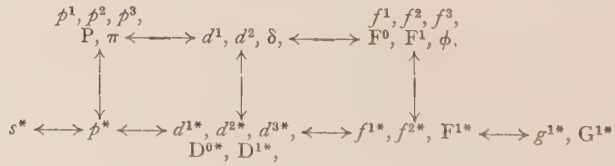
i	0	1	2	3	4
1	5898·28	5867·17	5804·45		
2		5936·99	5872·79	5775·04	
3			5934·42	5834·64	5696·36

Not one of these lines is to be found in the iron spectrum, and hence the new selection principle is confirmed.

Since the $d_i^1 - p_i^*$ transition is forbidden and since, further, the p^*-term lies deeper than the p^1- and d^{1*}-terms, the p^*-term, like the f^{1*} and F^{1*}-terms, is metastable, that is to say, an electron in a p^*-level cannot spontaneously return to the normal d^1-level.

The whole of the terms functioning in the iron spectrum can be arranged in the scheme shown in Table XCVI., where the transitions indicated by the horizontal and vertical arrows are alone possible.

TABLE XCVI.



In his first paper Laporte suggested that the terms p^1, p^2, p^3; d^{1*}, d^{2*}, d^{3*}; f^1, f^2, f^3, were consecutive members of the series *mp*, *md*, and *mf*. An entirely different explanation was proposed by Gieseler and Grotrian,[1] namely, that the terms d^1 and d^2 are $3d$ and $4d$ of a series *md*, and that the *p*-, d^*-, and *f*-terms are the first members of nine different series which have limits different from that of the *md* series. These nine terms were named "displaced" terms and Wentzel [2] suggested the name of double asterisk terms. As a strong argument in favour of d^1 and d^2 being $3d$ and $4d$, Gieseler and Grotrian gave a multiplet which they attributed to the combination $p_i{}^1 - 5d_i$. Assuming the reality of this multiplet, these authors find the very reasonable value for the ionisation potential, 8·15 volts, for which $\nu = 66000$. The septet δ would then become 4δ of the term series $m\delta$, the absence of 3δ being analogous to the absence of the triplet term $3s$ in the case of calcium.

Further, it would be possible to consider the terms f^{1*} and f^{2*} as $4f^*$ and $5f^*$ of the series mf^*. If it be assumed that $\infty d = \infty f^* = 66000$, then the terms $4f^*$ and $5f^*$ can be represented by a formula of the Ritz type.

It may thus be stated with respect to the levels of the various terms with the same azimuthal quantum numbers that the corresponding asterisk and non-asterisk terms are not similar. Rather is it that the terms p^*, d, f^*, and g are similar in that they are at a low level and show series relationships, whilst the single terms of the type s^*, p, d^*, f, and g^* lie near together at higher levels and thus are "displaced" in the sense of Gieseler and Grotrian.

TABLE XCVII.

19K	20Ca	21Sc	22Ti	23V	24Cr	25Mn	26Fe
	Singlet.		(Singlet.)		(Singlet.)		(Singlet.)
Doublet.		Doublet.		(Doublet.)		(Doublet.)	
	Triplet.		Triplet.		(Triplet.)		Triplet.
		Quartet.		Quartet.		Quartet.	
			Quintet.		Quintet.		Quintet.
				Sextet.		Sextet.	
					Septet.		Septet.
						Octet.	
							(Nonet.)

The multiple terms enclosed in brackets have not as yet been observed.

The recognition of the triplet, quintet, and septet terms functioning in the arc spectrum of iron completes the study of the permanent multiplicities of the elements in the third horizontal row of the periodic table. From the results described in the latter portion of this chapter it is necessary for us to recognise an obvious extension of Rydberg's law of alternation which stated that the elements in consecutive groups of the periodic table exhibit doublets and triplets alternately. We have already seen that the maximum multiplicity increases with the atomic weight in the horizontal row potassium to

[1] *Zeitsch. für Phys.*, **25**, 165 (1924). [2] *Ibid.*, **25**, 182 (1924).

manganese and, further, that the number of different multiplicities exhibited by the same element tends to increase with the atomic weight. We consequently arrive at the generalisation of Rydberg's law shown in Table XCVII. where each consecutive column shows the result of the binding of one additional electron.

Multiplets of Higher Order of Complexity.—In the preceding pages there have only been considered the multiplets of simple structure, which may be called multiplets of the first order. In these only the electrons of the lowest azimuthal quantum number ($k = 1$ in Sommerfeld's, $K = 1/2$ in Landé's enumeration) contribute to the moment of momentum of the atomic trunk, the electrons of the latter being bound as *s*-terms. If there are present in the atomic trunk electrons with $k > 1$, the terms still belong to the first order of complexity, provided that each contribution to the momentum $k > 1$ distributes itself equally, that is to say forms a closed shell without momentum. For this reason sodium, potassium, rubidium, and cæsium are spectroscopically similar to lithium, because they only differ by a closed shell of electrons. If, on the other hand, an electron for which $k > 1$ contributes to the moment of momentum R, in addition to the electrons for which $k = 1$, and one of these is bound as a *p*- or a *d*-term, then the atom exhibits multiplets of a second order. If two electrons for which $k > 1$ contribute to the moment of momentum of the atomic trunk, both being bound as *p*-terms, or one as a *p*-term and the other as a *d*-term, etc., then we have multiplets of the third order.

The one instance of a second order multiplet which has been resolved is that of neon, analysed by Paschen. It consists of a singlet system, two triplet systems, and a quintet system which are inter-connected. For the following description of the structure of this spectrum I am indebted to Back and Landé who give the values of I for the various terms which combine together,[1] the scheme being due to Landé.[2]

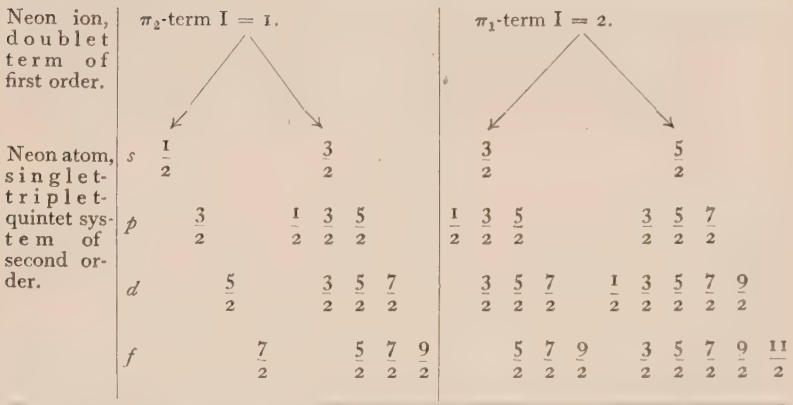
The structure is fundamentally based on a two-fold π-term of the neon ion, namely π_2 with $I = 1$ and π_1 with $I = 2$. As the result of the resolution or "branching" of these two terms, each with $I \rightarrow I \pm 1/2$, four *s*-terms are obtained of the second order for which $I = 1/2$, $3/2$, $3/2$, and $5/2$, respectively. The *s*-terms having $I = 1/2$, $3/2$, and $5/2$ give rise to singlet, triplet, and quintet systems respectively, and consequently there are formed one singlet system, two triplet systems, and one quintet system. The scheme is set out in Table XCVIII.

In general it will be seen that there are two pairs of systems, one having the π_2-term and the other the π_1-term as its basis. These pairs, according to Paschen's measurements, are separated by a wave-number interval of about 780 cm^{-1} and in the table these are divided by the vertical line.

[1] E. Back and A. Landé, *Zeemaneffekt und Multiplettstruktur der Spektrallinien*, p. 53, Springer, Berlin, 1925.

[2] *Zeitsch. für Phys.*, **17**, 292 (1923).

TABLE XCVIII.



In applying the symbolic methods of nomenclature n^r_{ki} introduced by Landé it is clear that several values of r must be used in the case of these spectral terms of the second order. For example, the neon terms which belong to the singlet-triplet-quintet systems must be indicated by the symbol n^{1335}_{ki}. In order to differentiate between the two pairs of systems, the terms derived from the π_2-

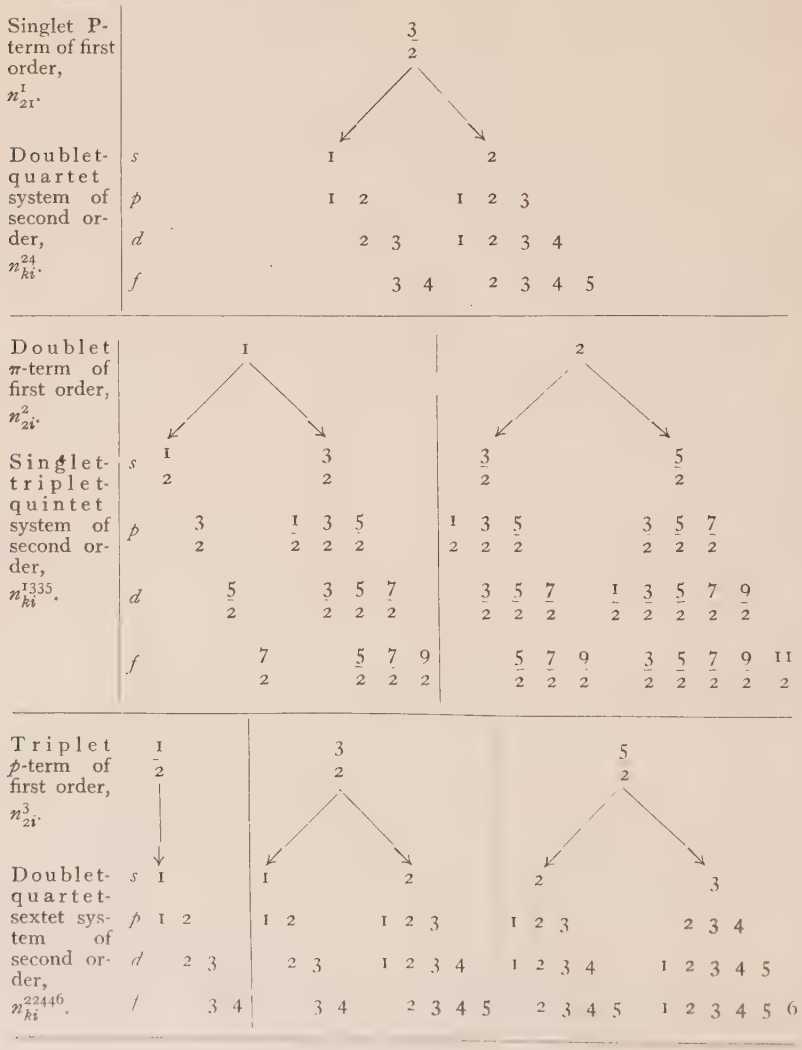
TABLE XCIX.

				s_3	s_2	s_4	s_5		
				n^{1335}_{10}	n^{1335}_{11}	n^{1335}_{11}	n^{1335}_{12}		
p_1	p_2	p_5	p_4	p_3	p_7	p_{10}	p_6	p_8	p_9
n^{1335}_{20}	n^{1335}_{21a}	n^{1335}_{21b}	n^{1335}_{22}	n^{1335}_{20}	n^{1335}_{21a}	n^{1335}_{21b}	n^{1335}_{22a}	n^{1335}_{22b}	n^{1335}_{23}
				s'_1	s''_1	s'''_1	s''''_1		
				n^{1335}_{31}	n^{1335}_{32a}	n^{1335}_{32b}	n^{1335}_{33}		
d_6	d_2	d_5	d''_1	d_3	d'_1	d_4	d'_4		
n^{1335}_{30}	n^{1335}_{31a}	n^{1335}_{31b}	n^{1335}_{32a}	n^{1335}_{32b}	n^{1335}_{33a}	n^{1335}_{33b}	n^{1335}_{34}		

term of the neon ion are indicated by n_{ki}^{1335} and the terms derived from the corresponding π_1-term by the symbol n_{ki}^{1335}. Furthermore, since there are always two terms of the same type, the suffixes *a* and *b* are used to indicate the smaller and larger terms respectively.

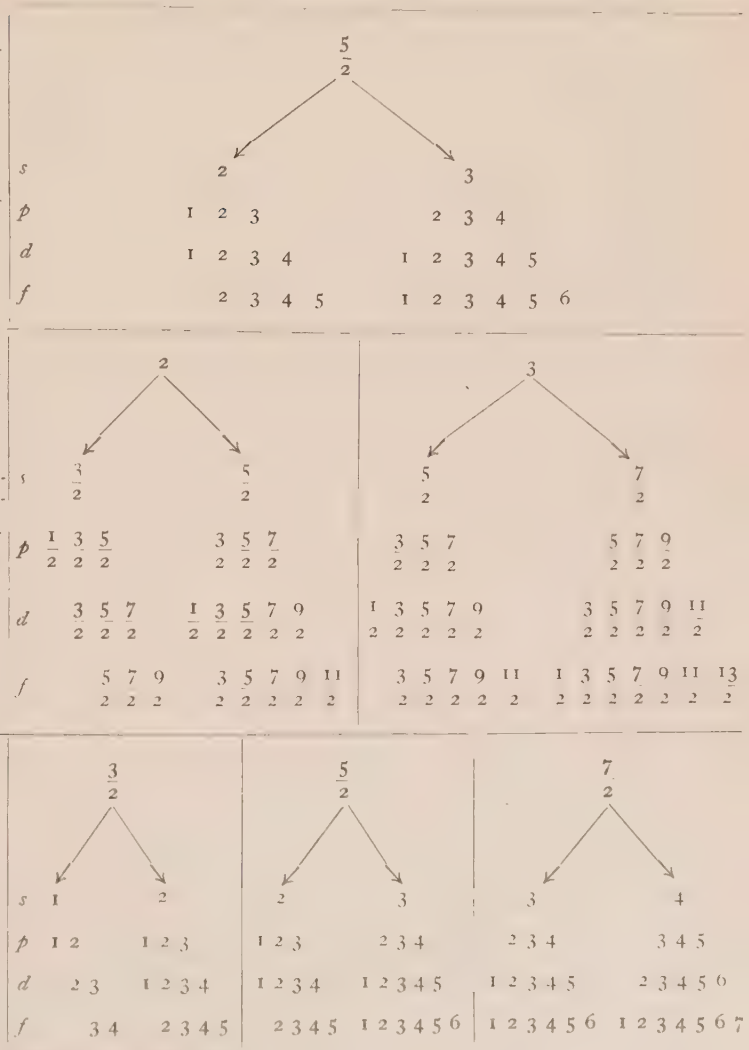
The various terms identified by Paschen are set out in Table XC1X. with the Landé symbols written underneath.

TABLE C.


Singlet P-term of first order, n_{21}^{1}.
Doublet-quartet system of second order, n_{ki}^{24}.
Doublet π-term of first order, n_{2i}^{2}.
Singlet-triplet-quintet system of second order, n_{ki}^{1335}.
Triplet p-term of first order, n_{2i}^{3}.
Doublet-quartet-sextet system of second order, n_{ki}^{22446}.
s
p
d
f

The system of terms derived for neon in Table XCVIII. by the branching of the two π-terms of the neon ion leads us to apply this principle of branching in a general way. Thus we may have systems of the second order established by the branching of a single, double, or triple p-term, or by the branching of a single, double, or triple d-term. The general scheme is set out in Tables C. and CI.

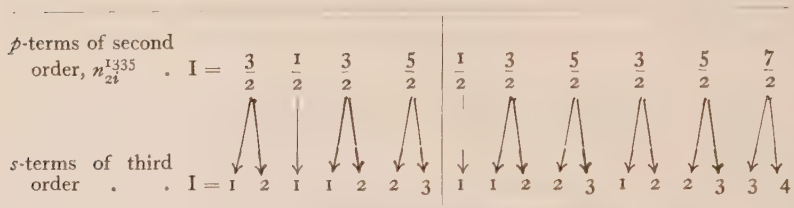
TABLE CI.


Singlet D-term of first order, n^{1}_{32}.
Quartet-sextet system of second order, n^{46}_{ki}.
Doublet δ-term of first order, n^{2}_{3i}.
Triplet-quintet-septet system of second order, n^{3557}_{ki}.
Triplet d-term of first order, n^{3}_{3i}.
Doublet-quartet-sextet-octet system of second order, n^{244668}_{ki}.
s
p
d
f

It must be noted that in the first member of the triplet p-term the branching of $I = 1/2$ leads to the values 0 and 1. Of these the value 0 is unreal and consequently only one branch is given.

The same principle may be applied to the terms of the second order whereby terms are obtained of the third order of complexity. For example, the ten neon p-terms of the second order would give eighteen s-terms of the third order according to the scheme set forth in Table CII.

TABLE CII.



There are thus obtained six s-terms with $I = 1$, seven with $I = 2$, four with $I = 3$, and one with $I = 4$. It follows that the spectrum of the third order will consist of six doublet systems, seven quartet systems, four sextet systems, and one octet system.

As has been already stated above, neon is the only example of a spectrum of a higher order of complexity than the first, which has as yet been analysed. As regards the ratios of wave-number differences and intensities, it must not be imagined that the resolution of the neon spectrum into a singlet-triplet system and a triplet-quintet system means that these obey the same laws as in spectra of the first order. This is by no means the case, since the neon spectrum must only be looked on as an arrangement of the values of I without any other commitments.

The four s-terms together form a narrow unit, as also do the ten p-terms, and these are so distributed that the terms with the Ne^+ π_2-term as origin are shifted with respect to the terms with the Ne^+ π_1-term as origin by about 780 cm.$^{-1}$. This shows the existence of certain simple laws. Since every term in the magnetic field is resolved into 2I components, we may give each term a weight equal to 2I. We now determine the "centre of gravity" of all the terms n_{ki}^{1335} which have the same values of n and k, giving each the weight of 2I, and also determining in the same way the centre of gravity of the terms n_{ki}^{1335} for the same values of n and k. Then if Paschen's values for the terms are used, it will be found that the two centres of gravity obtained with small values of n differ by an amount which is very near to 780 cm.$^{-1}$, although the convergence of the individual terms of two limits which differ by that amount can only be seen with higher values of n.

Back and Landé's general statement of the branching law may be given. If an atom is built up on energy states of its ion which are characterised by I_1, I_2, I_3 . . . I_m, the atom will then have $2m$ s-terms characterised by $I_1 \pm 1/2$, $I_2 \pm 1/2$ . . . $I_m \pm 1/2$ and will exhibit $2m$ systems with the multiplicities $2(I_1 \pm 1/2)$, $2(I_2 \pm 1/2)$ . . . $2(I_m \pm 1/2)$. When, however, $I_1 = 1/2$, then there is only one branch into $I + 1/2 = 1$ and in this case the atom will exhibit $2m - 1$ s-terms and $2m - 1$ interconnected multiplet systems. This law thus places Rydberg's law of alternation on a wider and more precise basis.

Back and Landé further say that the branching is characterised by the fact that the multiplet systems built up on a single state of the ion (*e.g.* the triplet-quintet system built up on the π_1-state of the neon ion) exhibit a special inter-relationship. These systems possess a common limit to the series of spectral terms. An example of this is afforded by the series of singlet terms and of triplet terms of cadmium, which arise from branching of the doublet σ-term of the cadmium ion, and which have the same series limit. Similarly, in the case of neon the series of triplet and quintet terms arising from the π_1-term of the neon ion have the same limit and this limit, as we have already seen, is displaced by 780 cm.$^{-1}$ with respect to the common limit of the singlet and triplet systems arising from the π_2-term of the neon ion. This may perhaps be better understood from Table CIII. in which are given Paschen's values of the various terms of each of the twelve d-series, the symbols (Paschen's and Landé's) for which were given in Table XCIX. The approach to one common limit for all the eight series of terms n_{3i}^{1335} and to another common limit for all the four series of terms n_{3i}^{1335} is clearly seen, the difference between the two limits being about 780. The same convergence to common limits for the n_{1i}^{1335} and n_{1i}^{1335} sequences, and for the n_{2i}^{1335} and the n_{2i}^{1335} sequences is shown by the values of the sequences given in Table CIV.

In order to complete the description of the structure of the neon spectrum it is only necessary to give the combinations which Paschen found between the various terms, and these are given in Table CV.

TABLE CIII.

m.	s_1 n_{31}^{1335}.	s_1'' n_{32a}^{1335}.	s_1'''' n_{32b}^{1335}.	s_1'' n_{33}^{1335}.	d_6 n_{30}^{1335}.	d_2 n_{31a}^{1335}.	d_5 n_{31b}^{1335}.	d_1'' n_{32a}^{1335}.	d_3 n_{32b}^{1335}.	d_1' n_{33a}^{1335}.	d_4 n_{33b}^{1335}.	d_4' n_{34}^{1335}.	m.
3	11493·777	11509·498	11520·818	11519·257	12419·875	12292·853	12405·233	12229·816	12322·259	12228·051	12337·323	12339·151	3
4	6121·687	6132·505	6134·473	6133·562	6961·797	6902·485	6954·126	6881·853	6917·919	6880·789	6928·369	6929·461	4
5	3633·432	3640·106	3640·473	3639·752	4446·443	4412·438	4441·035	4403·132	4420·888	4402·564	4427·148	4427·771	5
6	2284·565	2287·288	2289·452	2287·022	3081·236	3061·514	3078·128	3056·560	3066·464	3056·202	3070·547	3070·961	6
7	1468·399	1471·002	1471·550	1470·822	2260·272	2246·577	2257·525	2244·170	2248·114	2243·920	2253·703	2254·011	7
8	940·428	942·297	942·349	942·209	1729·075	1720·345	1727·573	1718·368	1722·661	1718·220	1724·170	1724·341	8
9	578·638	579·982	579·931	579·922	1364·545	1358·594	1363·532	1357·326	1360·060	1357·220	1361·431	1361·571	9
10	319·942	320·977	320·931	320·899	1104·860	1100·153	1103·978	1099·246	1101·547	1099·190	1102·214	1102·311	10
11	—	—	—	—	912·032	—	911·541	908·489	909·370	908·168	910·56	910·561	11
12	—	—	—	—	—	—	765·843	763·290	764·337	762·926	764·96	764·961	12
13	—	—	—	—	—	—	651·944	—	649·298	646·478	651·29	651·371	13

TABLE CIV.

m.	s_3 n_{10}^{1335}.	s_2 n_{11}^{1335}.	s_4 n_{11}^{1335}.	s_5 n_{12}^{1335}.	p_1 n_{20}^{1335}.	p_2 n_{21a}^{1335}.	p_5 n_{21b}^{1335}.	p_4 n_{22}^{1335}.	p_3 n_{20}^{1335}.	p_7 n_{21a}^{1335}.	p_{10} n_{21b}^{1335}.	p_6 n_{22a}^{1335}.	p_8 n_{22b}^{1335}.	p_9 n_{23}^{1335}.	m.
2	9110·508	38040·731	39470 160	39887·610	20958·718	22891·003	23157·342	23070·944	23012·015	23807·852	25671·654	23613·586	24105·229	24272·411	2
3	(11651·88)	(14505·53)	(15141·50)	(15332·17)	9643·510	10221·687	10272·127	10220·817	10528·095	10916·780	11411·490	10891·040	11030·293	11008·710	3
4	7325·132	7272·964	8016·679	8101·291	5342·445	5570·750	5573·896	5550·650	6062·146	6289·812	6479·926	6280·708	6338·150	6370·29	4
5	4223·467	4201·806	4962·103	5004·811	3240·040	3350·981	3344·458	3332·150	3952·655	4089·950	4181·293	4085·59	4114·714	4132·28	5
6	2616·576	2605·422	3372·371	3396·713	2015·95	2126·25	2107·1	2101·4	2780·615	2871·44	2920·09	2869·15	2885·75	2896·54	6
7	1675·101	1667·672	2439·967	2456·121	1264·31	—	1355·8	1356·0	2015·951?	2126·25	2156·5	2126·25	2137·8	2142·4	7
8	1077·331	1072·452	1848·546	1858·065	747·9	—	864·0	—	1602·1	1638·0	—	1638·0	1642·6	1647·2	8
9	674·195	670·006	1447·593	1454·136	422·9	—	—	—	—	1299·2	—	1299·2	—	1306·2	9
10	403·51	400·011	1164·914	1169·614	232·8	—	—	—	—	1057·5	—	1057·5	—	—	10
11	—	—	957·058	960·902	115·4	—	—	—	—	—	—	—	—	—	11
12	—	—	800·659	803·40	—	—	—	—	—	—	—	—	—	—	12

TABLE CV.

Principal Series.

$2s_2 - mp_1$	$m = 2, 3, 4, 5, 6, 7, 8, 9, 10, 11.$	$2s_3 - mp_2$	$m = 2, 3, 4, 5.$
$2s_2 - mp_2$	$m = 2, 3, 4, 5.$	$2s_3 - mp_5$	$m = 2, 3, 4, 5, 6, 7, 8.$
$2s_2 - mp_3$	$m = 2, 3, 4, 5, 6, 7, 8.$	$2s_3 - mp_7$	$m = 2, 4, 5, 6.$
$2s_2 - mp_4$	$m = 2, 3, 4, 5, 6.$	$2s_3 - mp_{10}$	$m = 2, 3, 4, 5, 6.$
$2s_2 - mp_5$	$m = 2, 3, 4, 5, 6.$		
$2s_2 - mp_6$	$m = 2, 3, 4.$		
$2s_2 - mp_7$	$m = 2, 3, 4, 5, 6.$		
$2s_2 - mp_8$	$m = 2, 3, 4, 5, 6.$		
$2s_2 - mp_{10}$	$m = 2, 3, 4, 5, 6.$		
$2s_4 - mp_1$	$m = 2, 3, 4, 5, 6, 7.$	$2s_5 - mp_2$	$m = 2, 3, 4, 5, 6.$
$2s_4 - mp_2$	$m = 2, 3, 4, 5, 6.$	$2s_5 - mp_4$	$m = 2, 3, 4, 5, 6, 7.$
$2s_4 - mp_3$	$m = 2, 3, 4, 5, 6, 7, 8.$	$2s_5 - mp_5$	$m = 2, 3, 4, 5, 6, 7, 8.$
$2s_4 - mp_4$	$m = 2, 3, 4, 5, 6, 7.$	$2s_5 - mp_6$	$m = 2, 3, 4, 5, 6, 7, 8, 9, 10.$
$2s_4 - mp_5$	$m = 2, 3, 4, 5, 6, 7, 8.$	$2s_5 - mp_7$	$m = 2, 3, 4, 5, 6, 7, 8, 9, 10.$
$2s_4 - mp_6$	$m = 2, 3, 4, 5, 6, 7, 8, 9.$	$2s_5 - mp_8$	$m = 2, 3, 4, 5, 6, 7, 8.$
$2s_4 - mp_7$	$m = 2, 3, 4, 5, 6, 7, 8, 9.$	$2s_5 - mp_9$	$m = 2, 3, 4, 5, 6, 7, 8, 9.$
$2s_4 - mp_8$	$m = 2, 3, 4, 5, 6, 7.$	$2s_5 - mp_{10}$	$m = 2, 3, 4, 5, 6, 7.$
$2s_4 - mp_{10}$	$m = 2, 3, 4, 5, 6, 7.$		

Sharp Series.

$2p_1 - ms_2$	$m = 2, 4, 5, 6, 7.$	$2p_1 - ms_4$	$m = 2, 4, 5, 6.$
$2p_2 - ms_2$	$m = 2, 4, 5, 6, 7, 9, 10.$	$2p_2 - ms_4$	$m = 2, 4, 5, 6, 7.$
$2p_2 - ms_3$	$m = 2, 4, 5, 6, 7, 8, 9, 10.$	$2p_2 - ms_5$	$m = 2, 4, 5, 6, 7, 8.$
$2p_3 - ms_2$	$m = 2, 4, 5, 6, 7, 8.$	$2p_3 - ms_4$	$m = 2, 4, 5, 6, 7.$
$2p_4 - ms_2$	$m = 2, 4, 5, 6, 7, 8, 9.$	$2p_4 - ms_5$	$m = 2, 4, 5, 6, 7, 8, 9.$
$2p_5 - ms_2$	$m = 2, 4, 5, 6, 7, 8, 9.$	$2p_5 - ms_4$	$m = 2, 4, 5, 6, 7, 8, 9, 10.$
$2p_5 - ms_3$	$m = 2, 4, 5, 6, 7, 8, 9.$	$2p_5 - ms_5$	$m = 2, 4, 5, 6, 7, 8.$

TABLE CV.—*Continued.*

SHARP SERIES—*Continued.*

$2p_6 - ms_2$	$m = 2, 4, 5, 6, 7, 8, 9.$	$2p_6 - ms_4$	$m = 2, 4, 5, 6, 7, 8, 9, 10.$
		$2p_6 - ms_5$	$m = 2, 4, 5, 6, 7, 8, 9, 10, 11.$
$2p_7 - ms_2$	$m = 2, 4, 5, 6, 7, 8.$	$2p_7 - ms_4$	$m = 2, 4, 5, 6, 7, 8, 9, 10, 11.$
$2p_7 - ms_3$	$m = 2, 4, 5, 6, 7, 8, 9.$	$2p_7 - ms_5$	$m = 2, 4, 5, 6, 7, 8, 9.$
$2p_8 - ms_2$	$m = 2, 4, 5, 6, 7, 8.$	$2p_8 - ms_4$	$m = 2, 4, 5, 6, 7, 8, 9, 10, 11, 12.$
		$2p_8 - ms_5$	$m = 2, 4, 5, 6, 7, 8, 9, 10, 11.$
		$2p_9 - ms_5$	$m = 2, 4, 5, 6, 7, 8, 9, 10, 11, 12.$
$2p_{10} - ms_2$	$m = 2, 4, 5, 6, 7, 8, 9.$	$2p_{10} - ms_4$	$m = 2, 4, 5, 6, 7, 8, 9, 10, 11.$
$2p_{10} - ms_3$	$m = 2, 4, 5, 6, 7, 8, 9.$	$2p_{10} - ms_5$	$m = 2, 4, 5, 6, 7, 8, 9, 10, 11.$

DIFFUSE SERIES.

$2p_1 - ms_1'$	$m = 4, 5, 6, 7.$	$2p_2 - ms_1''$	$m = 3, 4, 5, 6, 7, 8.$
$2p_1 - md_2$	$m = 4, 5, 6.$	$2p_2 - ms_1''$	$m = 3, 4, 5.$
		$2p_2 - ms_1''''$	$m = 4, 5, 6, 7, 8, 9, 10.$
		$2p_2 - md_2'$	$m = 4, 5, 6, 7, 8.$
		$2p_2 - md_3'$	$m = 4, 5, 6, 7, 8, 9.$
		$2p_2 - md_5'$	$m = 4, 5, 6, 7, 8, 9.$
		$2p_2 - md_6'$	$m = 4, 5, 6, 7, 8, 9.$
$2p_3 - ms_1'$	$m = 3, 4, 5, 6, 7, 8, 9, 10.$	$2p_4 - ms_1'$	$m = 4, 5, 6, 7.$
$2p_3 - md_2$	$m = 4, 5, 6, 7, 8, 9, 10.$	$2p_4 - ms_1''$	$m = 3, 4, 5.$
$2p_3 - md_5$	$m = 4, 5, 6, 7, 8, 9.$	$2p_4 - ms_1'''$	$m = 3, 4, 5, 6, 7, 8, 9, 10.$
		$2p_4 - ms_1''''$	$m = 3, 4, 5, 6, 7, 9, 10.$
		$2p_4 - md_1'$	$m = 3, 4, 5, 6, 7, 8, 9, 10, 11.$
		$2p_4 - md_1''$	$m = 3, 4, 5.$
		$2p_4 - md_2$	$m = 4, 5, 6, 7.$
		$2p_4 - md_3$	$m = 4, 5, 6, 7, 8, 9.$
		$2p_4 - md_4$	$m = 3, 4, 5, 6, 7, 8, 9, 10.$
		$2p_4 - md_5$	$m = 4, 5, 6, 7, 8.$

TABLE CV.—*Continued.*

DIFFUSE SERIES—*Continued.*

$2p_5 - ms_1'$	$m = 4, 5, 6, 7.$
$2p_5 - ms_1''$	$m = 3, 4, 5, 6, 7, 8, 9, 10.$
$2p_5 - ms_1''''$	$m = 3, 4, 5, 6, 9, 10.$
$2p_5 - md_1''$	$m = 3, 4, 6, 7, 8, 9.$
$2p_5 - md_2$	$m = 3, 4, 5, 6, 7, 8, 9, 10.$
$2p_5 - md_3$	$m = 4, 5, 6, 7, 8, 9.$
$2p_5 - md_6$	$m = 3, 4, 6, 7, 8.$

$2p_6 - ms_1'$	$m = 3, 4, 5.$
$2p_6 - ms_1''$	$m = 3, 4.$
$2p_6 - ms_1'''$	$m = 3, 4, 5, 6, 7, 8, 9, 10.$
$2p_6 - ms_1''''$	$m = 3, 4, 5, 6, 7, 9, 10.$
$2p_6 - md_1'$	$m = 3, 4, 5, 6, 7, 8, 9, 10, 11, 12.$
$2p_6 - md_2$	$m = 3, 4, 5, 6, 7, 8, 9.$
$2p_6 - md_3$	$m = 3, 4, 5, 6, 7, 8, 9, 10.$
$2p_6 - md_4$	$m = 3, 4, 5, 6, 7, 8, 9, 10.$
$2p_6 - md_5$	$m = 4, 5, 6, 7, 8.$

$2p_7 - ms_1'$	$m = 3, 4, 5, 6, 7, 8, 9.$
$2p_7 - ms_1''$	$m = 3, 4, 5, 6, 7, 8, 9, 10.$
$2p_7 - ms_1''''$	$m = 3, 4, 5, 6, 9, 10.$
$2p_7 - md_1''$	$m = 3, 4, 5, 6, 7, 8, 9, 10, 11, 12.$
$2p_7 - md_2$	$m = 3, 4, 5, 6, 7, 8, 9, 10.$
$2p_7 - md_3$	$m = 3, 4, 5, 6, 7, 8, 9.$
$2p_7 - md_4$	$m = 4, 5.$
$2p_7 - md_6$	$m = 3, 4, 5, 6, 7, 8.$

$2p_8 - ms_1'$	$m = 3, 4, 5.$
$2p_8 - ms_1''$	$m = 3, 4, 6.$
$2p_8 - ms_1'''$	$m = 3, 4, 5, 6, 7, 8, 9, 10.$
$2p_8 - ms_1''''$	$m = 4, 5, 6, 9, 10.$
$2p_8 - md_1'$	$m = 3, 4, 5.$
$2p_8 - md_1''$	$m = 3, 4, 5, 6, 7, 8, 9, 10.$
$2p_8 - md_2$	$m = 3, 4, 5, 6, 7, 8, 9.$
$2p_8 - md_3$	$m = 3, 4, 5, 6, 7, 8, 9.$
$2p_8 - md_4$	$m = 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13.$
$2p_8 - md_5$	$m = 3, 4, 5, 6, 7, 8, 9.$

$2p_9 - ms_1''$	$m = 3, 4.$
$2p_9 - ms_1'''$	$m = 3, 4, 6.$
$2p_9 - md_1'$	$m = 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13.$
$2p_9 - md_1''$	$m = 3, 4, 5.$
$2p_9 - md_3$	$m = 3, 4, 5, 6, 7, 8, 9.$
$2p_9 - md_4$	$m = 3, 4, 5, 6.$
$2p_9 - md_4'$	$m = 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13.$

$2p_{10} - ms_1'$	$m = 3, 4, 5, 6, 7, 8, 9.$
$2p_{10} - ms_1''$	$m = 3, 4, 5, 6.$
$2p_{10} - ms_1''''$	$m = 3, 4, 5, 6, 7, 8, 9, 10.$
$2p_{10} - md_1''$	$m = 4, 5, 6, 7.$
$2p_{10} - md_2$	$m = 3, 4, 5, 6, 7, 8, 9.$
$2p_{10} - md_3$	$m = 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13.$
$2p_{10} - md_5$	$m = 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13.$
$2p_{10} - md_6$	$m = 3, 4, 5, 6, 7, 8, 9, 10, 11.$

More recently a modification of Landé's theory has been brought forward by Heisenberg, and this has been applied by R. H. Fowler and Hartree to the O II. spectrum which was analysed by A. Fowler. In order to understand the application of the Heisenberg theory to a complex spectrum we may first deal with the architecture of the O II. spectrum which consists of terms of even multiplicities, there being present both doublet and quartet terms. The complexity of this spectrum, however, is great and it is necessary to consider it in some detail.

Before commencing to discuss Fowler's results [1] it is necessary to mention the notation used by him. This is merely an adaptation of that used by Landé, namely, n^r_{ki}. In place of the symbol n_k the term symbols *ms*, *mp*, *md*, etc., are frequently used, the azimuthal quantum number, 1, 2, 3, etc., being understood. In a Rydberg sequence the individual terms are indicated by successive numerical values of *m*. In the O II. spectrum, however, only one such sequence has as yet been recognised, and in other cases, where more than one term of the same type appears, the largest is designated by the prefix *a*, the second largest by *b*, and so on. Terms of the same type are of course recognised by their multiplet combinations or by the Zeeman patterns.

The multiplicity is indicated by an index on the upper left side of the term symbol. Thus a^2d means the largest *d* term of the doublet system, and b^4p means the second largest *p*-term of the quartet system. This notation was first suggested by Russell and Saunders.[2] The individual levels of each term are indicated by subscripts which are the inner quantum numbers.

In the spectrum of O II. there appear combinations due to asterisk terms as well as normal terms, the former now being believed to be due to the simultaneous displacement of two electrons.[3] As was first indicated by Laporte, the combination between asterisk and non-asterisk terms occur when $\Delta k = 0$, but there is evidence that in some cases $\Delta k = \pm 2$, as for example in the combination sd^*.

In their work on the alkaline earth metals Russell and Saunders found additional terms which behave like the normal terms, but differ in that they do not form part of the regular Rydberg series. They denoted these by p'', d'', etc., and Fowler finds two such terms in the O II. spectrum, which one may denote by ap^{**} and bp^{**}.

Turning now to the detailed structure of the O II. spectrum elucidated by Fowler, it is probable that three of the *p*-terms form part of a Rydberg sequence. These are represented by the formula

$$mp_2 = \frac{4N}{\left(m + 0{\cdot}316331 - \dfrac{0{\cdot}310848}{m}\right)^2},$$

[1] *Proc. Roy. Soc.*, **110**, 476 (1924).
[2] *Astrophys. Journ.*, **61**, 66 (1925).
[3] See p. 290.

giving

$$2p_2 = 93952{\cdot}53,$$
$$3p_2 = 42504{\cdot}63,$$
$$4p_2 = 24419{\cdot}23.$$

Although these values cannot be considered as firmly established, they may be adopted, whilst the remaining terms may be derived from their combinations. If the above p-sequence is justified, then it seems possible that the term $1s$ will be the largest term of the doublet system. The value of $1p_2$ given by the formula is 433942, which is quite improbably large. On the other hand, the above values of $2p$ lead to $2s = 79078{\cdot}69$, and the corresponding value of $1s$ given by a simple Rydberg formula is 238816. Whilst this may be greatly in error, it represents an ionisation potential for O II. of 29·5 volts, which is not hopelessly inconsistent with the value of 31 volts deduced from stellar spectra.[1]

The terms of the doublet system which have so far been traced are given in Table CVI., it being understood that the values have been reached on the supposition that three of the p-terms form an ordinary sequence, having 4N as the series constant.

TABLE CVI.

TERMS OF THE DOUBLET SYSTEM.

		$\Delta\nu$.			$\Delta\nu$.
$1s_1$	(238816) [2]		as_1^*	87310·5	
$2s_1$	79078·69		bs_1^*	27398·5	
$2p_1$	94132·52	179·99	ap_1^*	68851·16	59·74
$2p_2$	93952·53		ap_2^*	68791·42	
$3p_1$	42692·15	187·53	bp_1^*	50540·8	46·6
$3p_2$	42504·62		bp_2^*	50494·2	
$4p_1$	24612·3	193·1			
$4p_2$	24419·2				
[3] ap_2^{**}	49590·80	113·99	[3] ad_3^*	76049·6	1·0
ap_1^{**}	49476·81		ad_2^*	76048·6	
bp_1^{**}	29231·39	2·36	bd_2^*	48618·42	51·97
bp_2^{**}	29229·03		bd_3^*	48565·45	
ad_2	71498·92	190·68	cd_2^*	29974·67	2·12
ad_3	71308·24		cd_3^*	29972·55	
[3] bd_3	53074·3	21·6	[3] dd_3^*	23734·7	0·8
bd_2	53052·7		dd_2^*	23733·9	

[1] R. H. Fowler and E. A. Milne, *Roy. Astronom. Soc., Monthly Notices*, **84**, 499 (1924); Miss C. Payne, *Harvard College Observatory Circ.*, No. 256 (1924).

[2] Extrapolated from $2s$.

[3] Inverted terms, i.e. $p_2 > p_1$, or $d_3 > d_2$.

The combinations of these doublet terms are given in Table CVII.

TABLE CVII.

DOUBLET COMBINATIONS.

$^2s\ ^2p$ *Combinations.*		$2s_1 = 79078{\cdot}69.$	
		$\Delta\nu$.	
$2p_2 - 2s_1$	= 14873·87 (5)	180·18	$2p_2$ = 93952·53
$2p_1 - 2s_1$	= 15054·05 (4)		$2p_1$ = 94132·52
$2s_1 - 3p_1$	= 36386·52 (6)	187·95	$3p_1$ = 42692·15
$2s_1 - 3p_2$	= 36574·47 (10)		$3p_2$ = 42504·62
$2s_1 - ap_2^{**}$	= 29487·92 (8)	113·94	ap_2^{**} = 49590·80
$2s_1 - ap_1^{**}$	= 29601·86 (7)		ap_1^{**} = 49476·81

^2d, ^2p, *and* $^2d\ ^2p^{**}$ *Combinations.*

Term values.		ad_3 71308·24	190·68	ad_2 71498·92	Combinations.
$2p_1$	= 94132·52			22633·60 (8)	
	179·99			179·98	$2p - ad$
$2p_2$	= 93952·53	22644·29 (10)	190·67	22453·62 (6)	
$3p_1$	= 42692·15			28806·74 (5)	
	187·53			187·47	$ad - 3p$
$3p_2$	= 42504·62	28803·50 (8)	190·71	28994·21 (5)	
$4p_1$	= 24612·3			[1] 46888·3 (5)	
	193·1				$ad - 4p$
$4p_2$	= 24419·2	[1] 46888·3 (5)		47079·7 (1)	
bp_1^{**}	= 29231·39			42267·7 (3)	
	2·36			2·2	$ad - bp^{**}$
bp_2^{**}	= 29229·03	42079·5 (4)	190·4	42269·9 (1)	
		bd_3 53052·7	21·6	bd_2 53074·3	
$2p_1$	= 94132·52	41079·6 (9)			
	179·99	179·8			$2p - bd$
$2p_2$	= 93952·53	40899·8 (5)	21·6	40878·2 (10)	
bp_1^{**}	= 29231·39	23821·44 (1)			
	2·36	(2·4)			$bd - bp^{**}$
bp_2^{**}	= 29229·03	(23823·8)	(21·6)	23845·42 (2)	

$^2s^*\ ^2p^*$ *Combinations.*

	$as^*_1 = 87310{\cdot}5.$	$bs^*_1 = 27398{\cdot}5.$	
$as_1^* - bp_1^*$	= 36769·5 (2)	46·9	bp_1^* = 50540·8
$as_1^* - bp_2^*$	= 36816·4 (3)		bp_2^* = 50494·2
$bp_2^* - bs_1^*$	= 23095·58 (2)	46·46	
$bp_1^* - bs_1^*$	= 23142·04 (1)		
$ap_2^* - bs_1^*$	= 41393·0 (3)	59·9	ap_2^* = 68791·42
$ap_1^* - bs_1^*$	= 41452·9 (3)		ap_1^* = 68851·16

[1] Not resolved.

TABLE CVII.—*Continued.*

$^2p^*$ $^2d^*$ Combinations.

Term values.	ap_2^* 68791·42	59·74	ap_1^* 68851·16	Combinations.
$bd_2^* = 48618{\cdot}42$	20172·84 (3)	59·86	20232·70 (5)	
51·97	51·92			$ap^* - bd^*$
$bd_3^* = 48565{\cdot}45$	20224·76 (7)			
$cd_2^* = 29974{\cdot}67$	38816·65 (1)	59·89	38876·54 (4)	
2·12	2·15			$ap^* - cd^*$
$cd_3^* = 29972{\cdot}55$	38818·80 (6)			
$dd_3^* = 23734{\cdot}7$	45056·8 (2)			
0·8	(0·8)			$ap^* - dd^*$
$dd_2^* = 23733{\cdot}9$	(45057·6)	(59·8)	45117·4 (1)	
	$bp_2^* = 50494{\cdot}2$	46·6	$bp_1^* = 50540{\cdot}8$	
$ad_3^* = 76049{\cdot}6$	25555·48 (10)			
1·0	0·89			$ad^* - bp^*$
$ad_2^* = 76048{\cdot}6$	25554·59 (2)	46·89	25507·70 (6)	
$cd_2^* = 29974{\cdot}67$	(20519·44)	46·60	20566·04 (3)	
2·12	(2·06)			$bp^* - cd^*$
$cd_3^* = 29972{\cdot}55$	20521·50 (5)			
$dd_3^* = 23734{\cdot}7$	26759·43 (3)			
0·8	(0·8)			$bp^* - dd^*$
$dd_2^* = 23733{\cdot}9$	(26760·2)	(46·6)	26806·78 (2)	

^2p $^2p^*$ and $^2p^*$ $^2p^{**}$ Combinations.

Term values.	ap_2^* 68791·42	59·74	ap_1^* 68851·16	Combinations.
$2p_1 = 94132{\cdot}52$	25341·10 (5)	59·74	25281·36 (7)	
179·99	179·98		179·99	$2p - ap^*$
$2p_2 = 93952{\cdot}53$	25161·12 (10)	59·75	25101·37 (5)	
$3p_1 = 42692{\cdot}15$	26099·22 (4*r*)	59·88	26159·10 (4*r*)	
187·53	187·41		187·42	$ap^* - 3p$
$3p_2 = 42504{\cdot}62$	26286·63 (6*r*)	59·89	26346·52 (3*r*)	
$4p_1 = 24612{\cdot}3$	44179·3 (1)	59·3	44238·6 (2)	
193·1	194·1		192·0	$ap^* - 4p$ [1]
$4p_2 = 24419{\cdot}2$	44373·4 (3)	57·2	44430·6 (1)	
$ap_2^{**} = 49590{\cdot}80$	19200·58 (5)	59·82	19260·40 (3)	
113·99	113·99		113·99	$ap^* - ap^{**}$
$ap_1^{**} = 49476{\cdot}81$	19314·57 (2)	59·82	19374·39 (4)	
$bp_1^{**} = 29231{\cdot}39$	39560·2 (1)	59·6	39619·8 (3)	
2·36	2·2		2·2	$ap^* - bp^{**}$
$bp_2^{**} = 29229{\cdot}03$	39562·4 (4)	59·6	39622·0 (1)	

[1] Provisional wave-number.

Term values	bp_2^*		bp_1^*	Combinations.
$2p_1$ = 94132·52	50494·2	46·6	50540·8	
	43638·2 (4)	46·7	43591·5 (6)	
179·99	180·0		179·9	$2p - bp^*$
$2p_2$ = 93952·53	43458·2 (8)	46·6	43411·6 (5)	
bp_1^{**} = 29231·39	21262·70 (0)	46·63	21309·33 (1)	
2·36	2·40		2·27	$bp^* - bp^{**}$
bp_2^{**} = 29229·03	21265·10 (2)	46·50	21311·60 (0)	

$^2d\ ^2d^*$ *Combinations.*

Term values.	ad_3		ad_2	Combinations.
bd_2^* = 48618·42	22689·86 (1)	190·80	22880·66 (4)	
51·97	51·98		51·96	$ad - bd^*$
bd_3^* = 48565·45	22741·84 (7)	190·78	22932·62 (1)	
cd_2^* = 29974·67	41333·7 (1)	190·7	41524·4 (4)	
2·12	2·0		2·1	$ad - cd^*$
cd_3^* = 29972·55	41335·7 (6)	190·4	41526·5 (1)	
dd_3^* = 23734·7	47574·4 (4)			
0·8				$ad - dd^*$
dd_2^* = 23733·9	—		47765·3 (2)	
	bd_2		bd_3	
	53052·7	21·6	53074·3	
ad_3^* = 76049·6	(22996·9)		22975·33 (6)	
1·0				$ad^* - bd$
ad_2^* = 76048·6	22995·66 (5)	(21·6)	(22974·3)	
cd_2^* = 29974·67	23078·15 (2)	21·32	23099·47 (0)	
2·12	2·23		2·19	$bd - cd^*$
cd_3^* = 29972·55	23080·38 (0)	21·26	23101·66 (3)	
dd_3^* = 23734·7	(29318·0)		29339·68 (7n)	
0·8				
dd_2^* = 23733·9	29318·50 (6n)		(29340·4)	$bd - dd^*$

Attention should also be directed to the following lines of somewhat doubtful classification :—

Term values.	ad_3		ad_2	Combinations.
xd_3^* = 92582·48	21274·23 (7)	190·67	21083·56 (3)	
48·84	48·92		48·75	$xd^* - ad$
xd_2^* = 92533·64	21225·31 (5)	190·50	21034·81 (2)	

A few lines given by some of the expected combinations lie outside the region λ 6721 to λ 1850 investigated by Fowler, and these are not given in Table CVII. A notable exception, however, is the combination $ad - ap^{**}$ which should give lines in the blue region, none of which have been observed. Their absence may possibly be associated with the fact that the ap^{**} is an inverted term, suggesting a further restricting condition. The apparent absence of lines due to other combinations which are theoretically possible may generally

be attributed to their feeble intensities, since the smaller terms are involved.

The actual values of the terms of the quartet system have not been found. Assuming a value of 100,000 for the a^4p_3 level, the relative values of all the terms so far identified are given in Table CVIII. The term x_3 is of a type not yet identified, but it has the inner quantum number 3.

TABLE CVIII.

TERMS OF THE QUARTET SYSTEM.

Ordinary terms.	$\Delta\nu$.	Asterisk terms.	$\Delta\nu$.
$s_2 = 73337{\cdot}26$			
$ap_1 = 100263{\cdot}84$	105·32	$p_1^* = 77153{\cdot}03$	46·10
$ap_2 = 100158{\cdot}52$	158·52	$p_2^* = 77106{\cdot}93$	91·97
$ap_3 = 100000{\cdot}00$		$p_3^* = 77014{\cdot}96$	
$bp_1 = 46872{\cdot}88$	105·22		
$bp_2 = 46767{\cdot}66$	161·42		
$bp_3 = 46606{\cdot}24$			
$d_1 = 78768{\cdot}40$	55·54	$d_1^* = 52753{\cdot}69$	0·47
$d_2 = 78712{\cdot}86$	91·56	$d_2^* = 52753{\cdot}22$	1·53
$d_3 = 78621{\cdot}30$	124·62	$d_3^* = 52751{\cdot}69$	6·35
$d_4 = 78496{\cdot}68$		$d_4^* = 52745{\cdot}34$	
$f_2 = 54203{\cdot}15$	54·03		
$f_3 = 54149{\cdot}12$	77·91		
$f_4 = 54071{\cdot}21$	102·27		
$f_5 = 53968{\cdot}94$			

$x_3 = 52702{\cdot}93$

The combination of these quartet terms are shown in Table CIX. (see pp. 230 and 231).

The value of i_x which satisfies the above combinations is clearly 3, but the character of the x-term remains uncertain; it may be an unresolved ^4p- or $^4d^*$-term, or possibly a term of the sextet system.

The combination $^4s^4d^*$ also occurs, as will appear from the following :—

Calculated.	Observed.
$s_2 - d_1^* = 20583{\cdot}57$ $s_2 - d_2^* = 20584{\cdot}03$	20583·88 (3)
$s_2 - d_3^* = 20585{\cdot}56$	20585·27 (2)

The following lines involving already recognised values of $\Delta\nu$ may also be noted :—

23277·34 (3)	105·06	23978·50 (4)	91·92
23382·40 (4)		24070·42 (7)	55·42
		24125·84 (2)	

A very interesting paper has recently been published by R. H. Fowler and D. R. Hartree,[1] in which they apply to the above results

[1] *Proc. Roy. Soc.*, **111**, 83 (1926).

the theory of complex spectra brought forward by Heisenberg [1] and elaborated by Hund.[2] The agreement between the observed values and those indicated by the theory is most striking, almost all the theoretical terms giving strong lines in the region $\lambda = 6721$ to $\lambda = 1850$ are represented among the terms found by A. Fowler.

The definition of a complex spectrum as previously stated is the spectrum of an atom whose uncompleted n_k groups with $k > 1$ contain more than one electron. Fowler and Hartree give a brief statement of the Heisenberg and Hund theory which may be quoted here. In specifying the orbit of a single electron, five numbers may be used, n, k_1, k_2, m_1, and m_2. The significance of these numbers is as follows: n is the total quantum number, $k_1 = k - \frac{1}{2}$, where k is the azimuthal quantum number, $k_2 = k_1 \pm \frac{1}{2}$. It is more convenient to work with k_1 than k in building up the terms of complex spectra, but in referring to an orbit we may employ the symbol n_k. When there is only one electron not in a complete group, $k_2 = i + \frac{1}{2}$, if we adopt the Sommerfeld system of inner quantum numbers, that is to say, $i = 0$ for the s-term of a singlet system and $i = \frac{1}{2}$ for the s-term of a doublet system. Since i is usually interpreted as the angular momentum of the whole atom, it cannot generally be associated with a single electron in an orbit. The magnetic energy in a weak field is given by $m_1 g\omega h$ and in a strong field by $m_2\omega h$ [3] and in this way m_1 and m_2 are defined. For a single orbit only three of the quantum numbers $k_1 k_2$, m_1, m_2 are independent.

In calculating the terms of a complex spectrum it is necessary to take into account all the electrons in incomplete n_k groups. The spectroscopic nature of each term is specified by a quantum number l which relates to the whole set of electrons not in complete groups. It is not necessary that l is equal to the k_1 of any one of the orbits present, and it is taken to be 1/2, 3/2, 5/2, etc., for S, P, D, etc., terms, so that $l = k_1$ when there is only one electron in an incomplete group. Each term possesses a certain multiplicity $2r$, and is in general a multiple term with different levels defined by i, the values of i being uniquely determined by r and l.

In the terms which are given by a set of electrons in incomplete groups, the relation of r and l to the n_k of the individual electrons is obtained in the following way. The orbit of each n_k electron in a magnetic field is defined by the five quantum numbers n, k_1, k_2, m_1, and m_2, the magnetic state of each orbit is given by m_1 and m_2, and the magnetic state of a set of electrons is given by $m_1 = \Sigma m_1$, and

[1] *Zeitsch. für Phys.*, **32**, 841 (1925).

[2] *Ibid.*, **33**, 345 (1925); **34**, 296 (1925).

[3] An explanation of this will be found in Chapter II.; ω is Larmor's rotation frequency, h is the Planck constant, and g is the Landé separation given by

$$g = \tfrac{3}{2} + \frac{R^2 + K^2}{2(I^2 - \frac{1}{4})}$$

where R is one-half of the multiplicity of the system, K k_1 as defined above, and $I = i + \frac{1}{2}$.

TABLE CIX.

Quartet Combinations.

^4s ^4p Combinations.

$s_2 = 73337{\cdot}26.$

		$\Delta\nu$	
$ap_3 - s_2$	= 26662·74 (9)	158·52	$ap_3 = 100000{\cdot}00$
$ap_2 - s_2$	= 26821·26 (8)	105·32	$ap_2 = 100158{\cdot}52$
$ap_1 - s_2$	= 26926·58 (7)		$ap_1 = 100263{\cdot}84$
$s_2 - bp_1$	= 26464·35 (4r)	105·28	$bp_1 = 46872{\cdot}88$
$s_2 - bp_2$	= 26569·63 (5r)	161·35	$bp_2 = 46767{\cdot}66$
$s_2 - bp_3$	= 26730·98 (6r)		$bp_3 = 46606{\cdot}24$

^4d ^4p and ^4d ^4f Combinations.

Term Values.	d_4		d_3		d_2		d_1	
	78496·68	124·62	78621·30	91·56	78712·86	55·54	78768·40	
$ap_1 = 100263{\cdot}84$					21550·98 (6)	55·55	21495·43 (6)	
105·32					105·34		105·31	
$ap_2 = 100158{\cdot}52$			21537·23 (9)	91·59	21445·64 (9)	55·52	21390·12 (4)	
158·52			158·53		158·49			
$ap_3 = 100000{\cdot}00$	21503·32 (10)	124·62	21378·70 (8)	91·55	21287·15 (2)		($ap - d$)	
$bp_1 = 46872{\cdot}88$					31840·27 (4r)	55·37	31895·64 (3r)	
105·22					105·10		105·18	
$bp_2 = 46767{\cdot}66$			31853·78 (8r)	91·59	31945·37 (7r)	55·45	32000·82 (2r)	
161·42			161·36		161·38			
$bp_3 = 46606{\cdot}24$	31890·56 (10r)	124·58	32015·14 (6r)	91·61	32106·75 (1r)		($ad - bp$)	
$f_2 = 54203{\cdot}15$			24418·05 (0)	91·69	24509·74 (4)	55·57	24565·31 (4)	
54·03			54·15		53·96			
$f_3 = 54149{\cdot}12$	24347·57 (0)	124·63	24472·20 (3)	91·50	24563·70 (6)			
77·91	77·88		77·91					
$f_4 = 54071{\cdot}21$	24425·45 (5)	124·66	24550·11 (8)					
102·27	102·29							
$f_5 = 53968{\cdot}94$	24527·74 (10)						($d - f$)	

^4p $^4p^*$ Combinations.

Term Values.	p_3^* 77014·96		p_2^* 77106·93		p_1^* 77153·03	Combinations.
ap_1 = 100263·84			23156·88 (8)	46·08	23110·80 (3)	
105·32			105·18		105·30	
ap_2 = 100158·52	23143·55 (8)	91·85	23051·70 (6)	46·20	23005·50 (7)	$ap - p^*$
158·52	158·50		158·61			
ap_3 = 100000·00	22985·05 (8)	91·96	22893·09 (7)			
bp_1 = 46872·88			30233·87 (6r)	46·16	30280·03 (3r)	
105·22			105·25		105·19	
bp_2 = 46767·66	30247·13 (6r)	91·99	30339·12 (4r)	46·10	30385·22 (5r)	$p^* - bp$
161·42	161·55		161·41			
bp_3 = 46606·24	30408·68 (9r)	91·85	30500·53 (7r)			

$^4d^*$ $^4p^*$ and $^4d^*$ ^4d Combinations.

Term Values.	d_4^* 52745·34		d_3^* 52751·69		d_2^* 52753·22		d_1^* 52753·69
p_1^* = 77153·03					24399·76 (4)	0·42	24399·34 (1)
46·10					46·08		
p_2^* = 77106·93			24355·24 (5)	1·56	24353·68 (7)		(24353·26)$_1$
91·97			91·99		91·90		
p_3^* = 77014·96	24269·61 (8)	6·36	24263·25 (3)	1·47	24261·78 (2)		$(p^* - d^*)$
d_1 = 78768·40					26015·20 (3)		(26014·71)
55·54					55·51		
d_2 = 78712·86			25961·22 (2)	1·53	25959·69 (3)		(25959·17)
91·56			91·63		91·63		
d_3 = 78621·30	25875·96 (2)	6·37	25869·59 (5)	1·53	25868·06 (1)		
124·62	124·59		124·57				
d_4 = 78496·68	25751·37 (7)	6·35	25745·02 (3)				$(d - d^*)$

x ^4d, x $^4p^*$ and x ^4s Combinations.

$x_3 = 52702·93.$

	$\Delta\nu$	
$d_4 - x_3$ = 25793·70 (4)	124·65	d_4 = 78496·68
$d_3 - x_3$ = 25918·35 (4)	91·70	d_3 = 78621·30
$d_2 - x_3$ = 26010·05 (3)		d_2 = 78712·86
$p_3^* - x_3$ = 24312·00 (4)	91·98	p_3^* = 77014·96
$p_2^* - x_3$ = 24403·98 (3)		p_2^* = 77106·93

$\bar{m}_2 = \Sigma m_2$. Each separate electron can take all its possible magnetic states, subject to the condition that no two electrons can have the same values for all of the five quantum numbers. The separate magnetic states defined by $\bar{m}_1$ and m_2 are then collected into sets corresponding to the magnetic states of terms with various values of r, l, and i. For example, an n_2 orbit ($k_1 = \frac{3}{2}$) has six possible magnetic states

$$k_1 = \tfrac{3}{2}\begin{cases} m_1 = -\tfrac{1}{2} + \tfrac{1}{2} \\ m_2 = -1 \quad 0 \end{cases} \qquad \begin{matrix} k_2 = 1 \\ \\ \end{matrix} \qquad \begin{matrix} k_2 = 2. \\ -\tfrac{3}{2} \quad -\tfrac{1}{2} \quad +\tfrac{1}{2} \quad +\tfrac{3}{2}, \\ -2 \quad 0 \quad +1 \quad +2. \end{matrix}$$

A system formed of an n_2 orbit and an $(n^1)_2$ orbit has thirty-six magnetic states when n is not equal to n^1, since each orbit has six magnetic states and each orbit can take each of them independently of the other. These thirty-six states have values of m_1 and m_2 which correspond to the magnetic states of six terms, namely, ^1S, ^1P, ^1D, ^3S, ^3P, and ^3D. If $n = n^1$ then twenty-one out of the thirty-six magnetic states of the system disappear, some because different states of the atom are then no longer produced by changing the value of n (k_1 k_2, m_1, and m_2 remaining the same), others because no two electrons can have the same values of k_1 k_2 m_1 and m_2 if they have the same value of n. The remaining fifteen magnetic states have values of m_1 and m_2 which correspond to the terms ^1S, ^1D, and ^3P.

It is not necessary always to go through the calculation of the magnetic states. The general theoretical rule holds that if an electron in an n_k orbit is added to an ion defined by $r = R$ and $l = L$ (n and k not both being equal to the n and k of an electron already present), a set of terms is obtained for which l and r are given by

$$2r = 2R \pm 1,$$
$$|\, L - k_1 \,| + \tfrac{1}{2} \leqslant l \leqslant L + k_1 - \tfrac{1}{2}.$$

For example, if a 3_2 electron ($k_1 = \frac{3}{2}$) is added to an ion having complete 1_1 and 2_1 groups and two 2_2 orbits giving a ^3P state ($2R = 3$, $L = \frac{3}{2}$), then $2r = 2$ and 4, $l = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}$. The following states, therefore, are formed: ^2S, ^2P, ^2D, ^4S, ^4P, and ^4D. In order to find which of these terms remain when the value of n for the added electron is equal to that of one of the electrons already present, it is necessary to calculate the magnetic states of the orbits.

It may be stated as an empirical rule that of the terms based on a given state of the ion and a given n_k orbit of the added electron, those with greater values of l and r usually lie deeper than those with smaller values of l and r.

It is not possible to correlate uniquely the states of an atom with the values of k_2 of the orbits of the individual electrons in incomplete groups, but if the states are due to the addition of an electron to an ion in a state giving a multiple term, the individual members of the resulting multiple terms can be correlated with individual members

of the multiple term of the ion from which they were derived. This and this only is physically significant, and probably it is only significant when the single electron is in an orbit from which it can be removed much more easily than the electrons in the ion.

In the example given above, the correlation is shown in Table CX.

TABLE CX.

Ion.			Atom.							
Orbits.		Terms.	Orbits.			Terms.					
2_2	2_2	$^3P_2$	2_2	2_2	3_2	$^4D_4$	$^4P_3$	$^4S_2$	$^2D_3$	$^2P_2$	$^2S_1$
		$^3P_1$				$^4D_3$	$^4P_2$	$^4P_1$	$^2D_2$	$^2P_1$	
		$^3P_0$				$^4D_2$	$^4D_1$				

The rules of combination are as follows :—

1. Not more than two electrons make transitions from one n_k orbit to another, and then only such transitions occur for which $\Delta k_1 = \pm 1$ for one electron and $\Delta k_1 = 0, \pm 2$ for the other.

2. The terms can be divided into two classes, which may be written with and without a bar over the letters which specify the l value, *i.e.* S, P, D, etc. Within one class the transitions are restricted to those in which $\Delta l = \pm 1$, and occasionally ± 3. Between two classes the restriction is $\Delta l = 0$ and occasionally ± 2. It is immaterial which class is indicated by a bar.

3. $\Delta i = 0, \pm 1$, the transition $i \rightarrow i = 0 \rightarrow 0$ being excluded.

Up to the present we have distinguished the two classes of terms by the use of an asterisk, but we may follow Fowler and Hartree in using the bar here since this only refers to the combinations of the terms, whereas the asterisk has at times been used to indicate something further as, for example, a failure to fall into a Rydberg series.

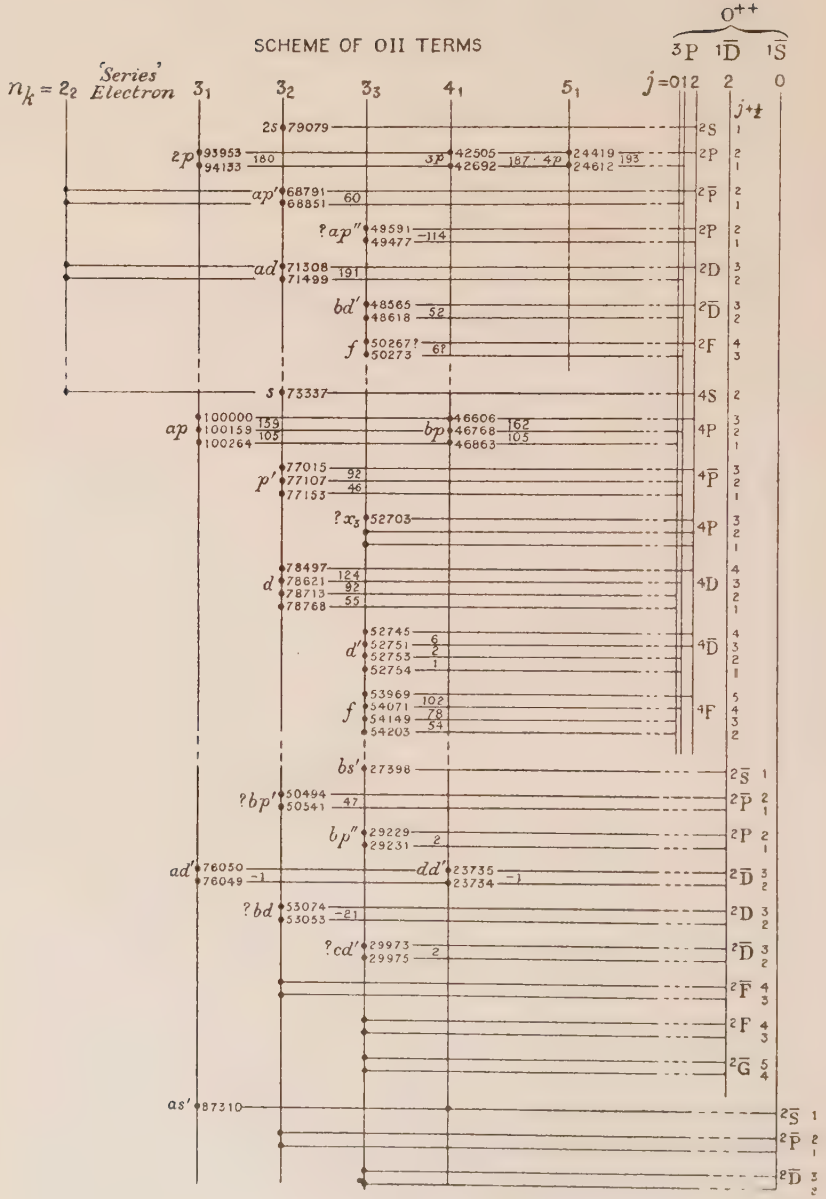
In applying this theory to the spectrum of O II., Fowler and Hartree point out that presumably the distribution of the electrons among the groups of the n_k orbits of the doubly-ionised oxygen atom is

$$2\ 1_1, \qquad 2\ 2_1, \qquad 2\ 2_2,$$

which gives the terms ^3P, ^1D, and ^1S, of which ^3P is probably deeper than ^1D, the $^1\bar{D}$ and $^1\bar{S}$ states being metastable. The O II. spectrum would therefore be expected to include mainly terms based on a ^3P state of the core, with some based on a ^1D state, and perhaps some based on a ^1S state.

In Table CXI. are shown the terms to be expected from the theory and the observed terms which have been correlated with them.

TABLE CXI.


SCHEME OF OII TERMS
O^{++}
^3P $^1\bar{D}$ ^1S
$n_k = 2_2$ 'Series' Electron 3_1 3_2 3_3 4_1 5_1 j=0 1 2 2 0
$j+\frac{1}{2}$
2s 79079 ^2S
2p 93953 94133 180 3p 42505 42692 187 4p 24419 24612 193 ^2P
ap' 68791 68851 60 $^2\bar{P}$
?ap'' 49591 49477 −114 ^2P
ad 71308 71499 191 ^2D
bd' 48565 48618 52 $^2\bar{D}$
f 50267? 50273 6? ^2F
s 73337 ^4S
ap 100000 100159 100264 159 105 bp 46606 46768 46863 162 105 ^4P
p' 77015 77107 77153 92 46 $^4\bar{P}$
?x_3 52703 ^4P
d 78497 78621 78713 78768 124 92 55 ^4D
d' 52745 52751 52753 52754 6 2 1 $^4\bar{D}$
f 53969 54071 54149 54203 102 78 54 ^4F
bs' 27398 $^2\bar{S}$
?bp' 50494 50541 47 $^2\bar{P}$
bp'' 29229 29231 2 ^2P
ad' 76050 76049 −1 dd' 23735 23734 −1 $^2\bar{D}$
?bd 53074 53053 −21 ^2D
?cd' 29973 29975 2 $^2\bar{D}$
$^2\bar{F}$
^2F
$^2\bar{G}$
as' 87310 $^2\bar{S}$ $^2\bar{P}$ $^2\bar{D}$

The vertical lines on the right of the table indicate the three states of the O^{++} core, the ^3P state being shown as resolved. From these a series of horizontal lines are drawn which are intersected by a series of vertical lines, some of the points of intersection being marked with dots. Each dot indicates a member of a multiple term derived from the theory, those on the same vertical line indicating the members due to the same n_k orbit of the added electron. The values of n_k are given at the top of these vertical lines. The dots on any one horizontal line represent individual levels of a multiple term, with the same values of r, l, and i, produced by adding an electron in an orbit with a given value of k but varying n to the O^{++} core in the state represented by the vertical line on the right in which the horizontal line has its origin. Thus the dots on the second and third horizontal lines indicate respectively $^2P_2$ and $^2P_1$ terms arising from the addition of an electron in an n_1 orbit to the O^{++} core in the $^3P_2$ and $^3P_1$ states. The horizontal lines for the members of a single resultant multiple term are grouped together.

The numbers on the right of the dots are the term values given by A. Fowler, which have been identified with the theoretical terms. All of his terms are represented in the diagram, except the somewhat doubtful xd^* doublet term 92582 and 92533.

Fowler and Hartree discuss these results and point out that there seem to be the beginnings of three Rydberg sequences among the observed terms. The most definite is the ^2P sequence formed by the addition of n_1 orbits to the ^3P state of the core. Each of these ^2P terms consists of two members based on the $^3P_1$ and $^3P_2$ states, respectively. Since the value of k of the added orbit is 1, it would be expected that the separations of the doublets would be all about the same and tend to the difference between the $^3P_1$ and $^3P_2$ states of the core as the value of n of the added orbit increases. This seems to be true, the three observed ^2P terms have separations of 180, 187, and 193, whilst the separation of the $^3P_1$ and $^3P_2$ states is probably about 204, this value being derived from Millikan and Bowen's observations of the triplet at $\lambda = 703$ which is provisionally adopted as an O III. triplet involving the ^3P state.

Fowler's quartet terms, ap and bp, probably also form the beginning of a Rydberg sequence, and consequently the separation of this series should tend towards the separations of the ^3P state, *i.e.* 107 and 204, as the value of n of the added orbit increases. When n is small it is to be expected that they would agree more nearly with the ratio 3 : 5 given by the Landé rule. The observed separations are 105, 158, and 105, 161, and, whilst the separation 105 is in agreement with the smaller separation of the ^3P state, the ratio 158 : 161 is much smaller than 3 : 5.

It also seems possible that the observed terms, ad^* and dd^*, are the first two members of a Rydberg series, and Fowler and Hartree give reasons in favour of this. They also point to the interesting values of the terms arising from the addition of a 3_3 orbit to the various

states of the core. The term value of a 3_3 orbit in the field of a point charge 2 is $4N/g = 48772$. If in O^+ the 3_3 orbit lies entirely outside the core, as would be expected from a consideration of orbital dimensions, the terms due to the addition of it to the core should have about this value (reckoned from the appropriate state of the core). As a matter of fact the terms identified as being due to the addition of the 3_3 orbit have values which are close to 48772, but rather greater on the whole, as perhaps might be expected from analogy with simpler spectra. Further, the separations of the *bp** and *cd** doublets, due to the addition of 3_3 orbit to the $^1\bar{D}$ state of the core, are both small. This perhaps might be expected, since the external 3_3 orbit is not likely, broadly speaking, to contribute much to the separation, and the singlet state of the core has no separation which can be affected. On the other hand, as has been shown by Heisenberg, the addition of an electron even in an external orbit (with R = 1) may considerably affect the separations when the core is not in a state that gives a singlet term.

The definite absence of the combination *ad* — *ap***, and the large negative separation of the *ap*** term throws doubt on the identification of this term, but there seems little prospect of explaining it in any other way on the present theory. It must not be forgotten that terms based on other O III. states may occur; the deepest would be a $^2\bar{P}$ term due to the electron arrangement 2_2, 3_1, 3_1 (in addition to the electrons in completed 1_1 and 2_1 groups), and the next a group of terms (including a ^2P term) due to the arrangement 2_2, 3_1, 3_2, but these terms would be expected to be very much smaller than the observed *ap*** terms.

The Electronic Orbits of the Elementary Atoms.—There is one extension of the Bohr theory of the atom which we have not hitherto touched upon in any way. Whilst it would be beyond the scope of the present chapter to enter into a full discussion of the applications of this theory, however great the temptation, one particular section of Bohr's investigations does perhaps concern us, namely, the successive capture and binding of the electrons, one by one, in the field of force surrounding the nucleus. Whereas the problem is simple enough in the case of the hydrogen atom with its single electron, the conditions obtaining with the other elements naturally become more complex.

For an element of the atomic number A the formation of the normal atom by the return of the displaced electrons must consist of A separate stages, to each of which binding process there must correspond a spectrum.[1] As regards these spectra, those of hydrogen and helium are the only ones about which we have any detailed knowledge. As regards the other elements of higher atomic number we know that their spectra consist of different types, arc spectra and spark spectra, according to the method of excitation Leaving on

[1] *The Theory of Spectra and Atomic Constitution*, p. 75 *et seq.*, N. Bohr, Cambridge University Press, 1924.

one side the fact that all such spectra consist of even or uneven systems of multiplicities we know that all spectrum lines can be expressed as the difference of two terms, which on Bohr's theory represents the energy difference between two stationary states of the atom. The expression of the spectral line frequencies as the difference of two terms was first established by Rydberg and generalised by Ritz in his combination principle. The Rydberg formula can be written in the general form

$$n = \frac{N}{(r_1 + a_{k_1})^2} - \frac{N}{(r_2 + a_{k_2})^2}$$

where a_{k_1} and a_{k_2} are constants characteristic of the elements and of each particular series. It is now known that this formula is only approximate, since a_{k_1} and a_{k_2} are not constant, but with increasing values of r_1 and r_2 approach a constant limiting value. Since it is now known that spark spectra are exactly analogous to arc spectra when N in the above formula is replaced by 4N, 9N, 16N, etc., we may assume that arc spectra are connected with the last stage in the formation of the neutral atom, that is to say, the binding of the Ath electron. Similarly we may assume that the spark spectrum expressed by a formula containing 4N is connected with the binding of the (A — 1)th electron, and so on. Following on this we may, if we neglect the Sommerfeld fine structure of the individual lines, write the energy of the atom in the rth state of the kth series as

$$F_k(r) = -\frac{xNh}{(r + a_k)^2},$$

where $x = 1$ for arc series and 4 for the first spark series, and so on.

As has been previously shown the orbit of the electron is defined by two numbers, the radial quantum number and the azimuthal quantum number, the sum of these two being the total quantum number of the orbit. We know from Sommerfeld's work that the azimuthal quantum numbers 1, 2, 3, and 4 are associated with the sharp, principal, diffuse, and fundamental series respectively. It follows, therefore, that whilst the azimuthal quantum number is constant within any given series the radial quantum number increases for the consecutive variable terms of a given series from the value required to complete the total quantum number of the first term up to infinity. As will be shown below the total quantum number of the first term of the sharp series of sodium is 3 and since the azimuthal quantum number of this series is 1, the orbit corresponding to the first term is represented by 3_1. The radial quantum numbers for the sequence of terms of the sharp series are 2, 3, 4, 5, etc. In general, therefore, orbits are defined by the total quantum number n and those having the same total quantum number are differentiated by the azimuthal quantum number k in the symbol n_k.

It is an obvious assumption that the final stage of the binding of the first electron in any atom will be a stationary state where

the orbit of the electron is a 1-quantum orbit, and consequently it may be said that in the neutral hydrogen atom the electron moves in a 1-quantum orbit, or more precisely a 1_1 orbit. In the case of helium we have the more complicated problem of the binding of the second electron which gives rise to the arc spectrum of helium. As is well known this spectrum consists of two systems of lines, each of which can be expressed by series formulæ, and for this reason it was originally believed that helium consisted of a mixture of two gases, helium and parhelium. The application of the Bohr theory, however, has shown, as the result of Franck's work on dissociation potentials, that the explanation of the two spectra is to be found in the fact that the binding of the second electron can take place in two ways. By one method the normal helium atom is produced, this process giving the parhelium spectrum, whilst the second method, associated with the helium spectrum, gives a metastable helium atom which cannot by a simple transition involving radiation change into the normal atom. In the former case the electron last captured, as well as the first one captured, is bound in a 1_1 orbit. In the latter case the second electron differs from the first and is bound in a 2_1 orbit, in which the firmness of binding is about six times less than that in the normal state of the atom.

In the case of the elements which possess more than two electrons in the neutral state, it may be assumed that the binding of the first two electrons will in the main be similar to that in the formation of the neutral helium atom. These two electrons, therefore, may in the normal state of the atom be considered as moving in equivalent 1_1 orbits. For the binding of the third electron we look for information to the arc spectrum of lithium and also to its absorption spectrum. From the former we learn of the existence of a number of stationary states, where the firmness with which the last captured electron is bound is very nearly the same as in the stationary states of the hydrogen atom. These correspond to orbits where the azimuthal quantum number k is greater than or equal to 2, and the last captured electron moves entirely outside the region where the first two electrons move. In addition, there exists a series of states where $k = 1$ in which the last captured electron, even if it remains at a considerable distance from the nucleus during the greater part of its revolution, will at times approach to a distance from the nucleus which is comparable to the dimensions of the orbits of the first two electrons. For this reason the electrons will be bound with a firmness considerably greater than that binding the electrons in the stationary states of the hydrogen atom with the same value of n.

Again, it is known that the absorption spectra of the alkali metals exhibit the principal series of lines which means that the normal state of the lithium atom corresponds to the first member of the sharp sequence, since the general formula of the principal series is $1S - n\mathrm{P}$. This term corresponds to a strength of binding which is only a little more than one-third of that of the hydrogen atom. It

may therefore be concluded that the outer electron of the normal lithium atom moves in a 2_1 orbit just as the outer electron in the metastable state of the helium atom.

It may be noted in passing that this arrangement offers an explanation of the difference in properties between lithium and hydrogen or helium. There is one electron readily lost which makes it electropositive like hydrogen. The binding of this electron is one-third that of the hydrogen electron and one-fifth that of the helium atom.

Although little is known about the series spectra of the next elements, beryllium, boron, and carbon, and we have thereby no certain guide as to the binding of the 4th, 5th, and 6th electrons, Bohr first assumed that all these are bound in 2_1 orbits. Owing, however, to the discovery by Fowler of the enhanced spectrum of carbon (with series constant 4N) which involves the 5th electron, Bohr shows that it is necessary to assume that the 5th electron is bound in a 2_2 orbit, and the reason for this will be further explained below.

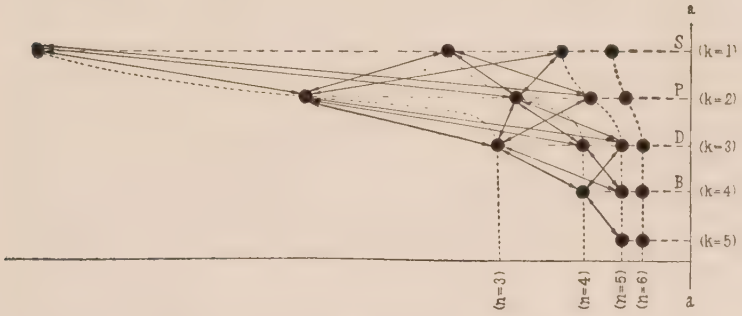


FIG. 23.

(From Bohr's "Theory of Spectra and Atomic Constitution." Cambridge University Press.)

From the point of view of spectral series the electronic orbits in the third period of the periodic table, including sodium, magnesium, aluminium, silicon, are of considerable importance. In the case of the first element sodium we have the problem of the binding of the 11th electron, that is to say, one more than in the case of neon. Bohr shows that the symmetry of the configuration in the neon atom, to which its characteristic properties are due, would be essentially, if not entirely, destroyed by the addition of another electron in an orbit of the same type as that of the outer neon electron. For this reason he considers that the 3 orbits come into being in the case of sodium. Just as in the case of lithium, the absorption spectrum of sodium exhibits a principal series of lines and therefore the first term in the sharp sequence may be assumed to correspond to a 3_1 orbit. He also shows that the first term of the principal series must correspond to a 3_2 orbit.

In Fig. 23 is shown a schematic representation of the stationary states of the electrons of sodium, which give rise to the series spectra

of that element. The black dots represent the stationary states, and the distance of these from the vertical line *aa* is proportional to the numerical value of the energy given by equation (35) above. The arrows indicate the various transitions which give rise to the individual spectrum lines. The states in the first horizontal row S represent the variable term in the sharp series, the lines in which are given by transitions from these to the first term in the second row. The second row P gives the variable terms in the principal series, the lines of which are given by the transitions from these states to the first state in the S row. The D row contains the states corresponding to

FIG. 24.

(*From Bohr's "Theory of Spectra and Atomic Constitution." Cambridge University Press.*)

the diffuse series, the lines of which are given, like the sharp series, by transitions to the first state of the second row. Finally, the fourth row contains the terms of the fundamental series, the lines of which are given by transitions to the first state in the D row. The curved dotted lines join up the states having the same principal quantum number.

In the case of magnesium there is little doubt from its spectrum that the 12th electron is bound in a 3_1 orbit, similarly to the 11th electron, but in aluminium we come across a new phenomenon. The absorption spectrum of this element does not show the principal series but the sharp and diffuse series, and consequently it is obvious that

the 13th electron must be bound in an orbit corresponding to the first term of the principal series, *i.e.* a 3_2 orbit. This is also true of the 31st, 49th, and 81st electrons in the chemically analogous elements gallium, indium, and thallium respectively. Fig. 24 represents the stationary

TABLE CXII.

n_k	1	2 2	3 3 3	4 4 4 4	5 5 5 5 5	6 6 6 6 6 6	7 7
1 H	1						
2 He	2						
3 Li	2	1					
4 Be	2	2					
5 B	2	2 1					
10 Ne	2	[4 4]					
11 Na	2	4 4	1				
12 Mg	2	4 4	2				
13 Al	2	4 4	2 1				
18 A	2	4 4	[4 4]				
19 K	2	4 4	4 4	1			
20 Ca	2	4 4	4 4	2			
21 Sc	2	4 4	4 4 1	(2)			
22 Ti	2	4 4	4 4 2	(2)			
29 Cu	2	4 4	[6 6 6]	1			
30 Zn	2	4 4	6 6 6	2			
31 Ga	2	4 4	6 6 6	2 1			
36 Kr	2	4 4	6 6 6	[4 4]			
37 Rb	2	4 4	6 6 6	4 4	1		
38 Sr	2	4 4	6 6 6	4 4	2		
39 Y	2	4 4	6 6 6	4 4 1	(2)		
40 Zr	2	4 4	6 6 6	4 4 2	(2)		
47 Ag	2	4 4	6 6 6	[6 6 6]	1		
48 Cd	2	4 4	6 6 6	6 6 6	2		
49 In	2	4 4	6 6 6	6 6 6	2 1		
54 X	2	4 4	6 6 6	6 6 6	[4 4]		
55 Cs	2	4 4	6 6 6	6 6 6	4 4	1	
56 Ba	2	4 4	6 6 6	6 6 6	4 4	2	
57 La	2	4 4	6 6 6	6 6 6	4 4 1	(2)	
58 Ce	2	4 4	6 6 6	6 6 6 1	4 4 1	(2)	
59 Pr	2	4 4	6 6 6	6 6 6 2	4 4 1	(2)	
71 Cp	2	4 4	6 6 6	[8 8 8 8]	4 4 1	(2)	
72 Hf	2	4 4	6 6 6	8 8 8 8	4 4 2	(2)	
79 Au	2	4 4	6 6 6	8 8 8 8	[6 6 6]	1	
80 Hg	2	4 4	6 6 6	8 8 8 8	6 6 6	2	
81 Tl	2	4 4	6 6 6	8 8 8 8	6 6 6	2 1	
86 Nt	2	4 4	6 6 6	8 8 8 8	6 6 6	[4 4]	
87 —	2	4 4	6 6 6	8 8 8 8	6 6 6	4 4	1
88 Ra	2	4 4	6 6 6	8 8 8 8	6 6 6	4 4	2
89 Ac	2	4 4	6 6 6	8 8 8 8	6 6 6	4 4 1	(2)
90 Th	2	4 4	6 6 6	8 8 8 8	6 6 6	4 4 2	(2)
118 (?)	2	4 4	6 6 6	8 8 8 8	[8 8 8 8]	[6 6 6]	[4 4]

states of the electrons of these four elements, the arrangement being analogous to that in Fig. 23. The dotted vertical lines with various values of n (total quantum number) correspond to the spectral terms of hydrogen.

It was for the same reason that Bohr, basing his conclusion on Fowler's investigation of the enhanced spectrum of carbon, concluded that the 5th electron is bound in a 2_2 orbit, since the first term of the principal sequence is larger than the first term of the sharp sequence.

The general conclusions drawn by Bohr as to the classification of the orbits of the electrons in the elements are given in Table CXII., but it must be remembered that there are still unsolved difficulties and that the scheme must not be considered as final. In view of the great value of Bohr's work I feel no apology is needed for reproducing this table from his book. The square brackets indicate the first occurrence of a completed group of electrons having orbits of the same total quantum number. The inclusion of certain numbers in round brackets indicates that the experimental evidence is as yet insufficient to fix these numbers with certainty. In the first column the symbols of the elements are preceded by their atomic numbers whilst the top row indicates the orbits defined by the symbol n_k.

The Relativity Correction and the Fine Structure of Lines.—In concluding our discussion of the contributions made by Sommerfeld to the theory of spectral series, we may deal with his application of the principles of relativity to the Kepler motion. This is a question of considerable importance, but we cannot enter into the problem in more than an elementary way, that is to say, just so far as concerns the hydrogen and helium lines. It has long been known that these lines are not truly single lines, that is to say each does not consist of monochromatic radiation as has been tacitly assumed from the elementary form of the Bohr equation—

$$\nu = \mathrm{N}\left(\frac{1}{n^2} - \frac{1}{n_1^2}\right).$$

It was found by Michelson as far back as 1891 that these lines are certainly double,[1] and, from the point of view of the general theory of multiple systems of spectral series, this presents considerable difficulty. There is no question but that the hydrogen lines are not doublets of the same type as evidence themselves, for example, in the spectra of the alkali metals. The solution of this problem has been found in the relativity principle,[2] and when a correction in the formula is introduced for the variation in the mass of the electron with its velocity, the resulting formula not only establishes the double nature of the hydrogen lines, but also shows that each member of the pair consists of separate components. This is what is meant by the fine structure of the hydrogen lines.

[1] See vol. ii., p. 179.

[2] Sommerfeld, *Ann. der Phys.*, 51, 1 (1916); *Atombau und Spektrallinien*, p. 408.

Now in the Einstein relativity theory the mass of the electron is given by

$$m = \frac{m_0}{\sqrt{1 - \beta^2}} \quad . \quad . \quad . \quad . \quad (1)$$

where m_0 is the mass when the electron is at rest, that is to say, when $\beta = 0$, and β is the velocity of the electron measured in relation to the velocity of light. This value has to be introduced into our formulæ for the quantising of the Kepler ellipse which were developed on p. 105 *et seq.* It will be convenient to re-state the original conditions, which were two degrees of freedom, namely, the azimuth ϕ and the radius vector q. The quantum conditions are given by

$$\int_{\phi=0}^{\phi=2\pi} p_\phi d\phi = kh, \qquad \int_{\phi=0}^{\phi=2\pi} p_q dq = rh \quad . \quad . \quad . \quad (2)$$

where p_ϕ and p_q are the two impulse or momentum co-ordinates. By Kepler's second law p_ϕ is a constant during the motion, and we may therefore put

$$p_\phi = p,$$

and consequently the first equation in (2) becomes

$$2\pi p = kh \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The second equation in (2), expressed in terms of the orbital equation of the ellipse, becomes

$$\frac{1}{q} = C_1 + C_2 \cos \phi \quad . \quad . \quad . \quad (4)$$

Now relativistic Kepler motion takes place in an ellipse, the perihelion of which is advancing. This means that equation (4) becomes

$$\frac{1}{q} = C_1 + C_2 \cos \gamma\phi \quad . \quad . \quad . \quad . \quad (5)$$

where the factor γ has the meaning

$$\gamma^2 = 1 - \frac{p_0^2}{p^2} \quad . \quad . \quad . \quad . \quad (6)$$

In (6) p has the same meaning as before and

$$p_0 = \frac{e\mathrm{E}}{v} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where e is the charge on the electron, E the charge on the nucleus, and v is the velocity of light.

As the result of (5) the radial quantum condition stated in (2) must be modified, and, if we put $\psi = \gamma\phi$, we have for the two quantum conditions (azimuthal and radial)

$$\int_{\phi=0}^{\phi=2\pi} p_\phi d\phi = kh, \qquad \int_{\psi=0}^{\psi=2\pi} p_q dq = rh \quad . \quad . \quad . \quad (8)$$

The azimuthal quantum condition is the same as that previously and therefore we again have

$$2\pi p = kh \quad . \quad . \quad . \quad . \quad . \quad (9)$$

The radial quantum condition in (8) passes over into

$$\frac{\epsilon^2}{2\pi}\int_{\psi=0}^{\psi=2\pi} \frac{\sin^2\psi}{(1+\epsilon\cos\psi)^2}d\psi = \frac{r}{k\gamma} \quad . \quad . \quad (10)$$

where the integral on the left is identical with the integral in equation (3) on p. 105, except for the way the integral variables are designated. If we use the result previously obtained in evaluating the integral in (10) we have

$$\frac{1}{\sqrt{1-\epsilon^2}} = \frac{r}{k\gamma}$$

or

$$1-\epsilon^2 = \frac{k^2\gamma^2}{(r+k\gamma)^2} \quad . \quad . \quad . \quad . \quad (11)$$

Then from (6), (7), and (9)

$$k\gamma = \sqrt{k^2 - \frac{k^2 p_1^2}{p^2}} = \sqrt{k^2 - \left(\frac{2\pi e\mathrm{E}}{hv}\right)^2} = \sqrt{k^2 - a^2x^2} \quad . \quad (12)$$

where $a = 2\pi e^2/hv$ and $x = \mathrm{E}/e$.

As the result of (12) we have from (11)

$$1-\epsilon^2 = \frac{k^2 - a^2x^2}{(r+\sqrt{k^2-a^2x^2})^2} \quad . \quad . \quad . \quad (13)$$

In calculating the energy, Sommerfeld first deals with a circular orbit and then calculates the energy of the elliptical orbit with its two quantum numbers. Here it is that we have to take into account the fact that the mass of the electron varies with its velocity. We will deal with this question first. If a is the radius of the circular orbit and ω the angular velocity of the electron in that orbit, then

$$p = ma^2\omega = \frac{nh}{2\pi} \quad . \quad . \quad . \quad . \quad (14)$$

this being the only quantum condition which comes into consideration with circular orbits, n being the total quantum number. Since the centrifugal force is equal to the Coulomb attraction of the nucleus, we have in addition to the foregoing

$$ma^3\omega^2 = e\mathrm{E},$$

and consequently it follows from (14) that

$$a\omega = \frac{2\pi e\mathrm{E}}{nh} \quad . \quad . \quad . \quad . \quad (15)$$

This gives the velocity of the electron in its orbit and what we require for the relativity correction is the velocity measured in terms of the velocity of light. In order to obtain the latter we divide (15) by the velocity of light v, and thus we have

$$\beta = \frac{a\omega}{v} = \frac{2\pi e\mathrm{E}}{nhv} = \frac{a\mathrm{E}}{ne} = \frac{ax}{n} \quad . \quad . \quad . \quad (16)$$

Now, as already stated in (1), the mass m of the electron varies with its velocity in accordance with the relation

$$m = \frac{m_0}{\sqrt{1 - \beta^2}},$$

and substituting the value of β from (16) we have

$$m = \frac{m_0}{\sqrt{1 - \frac{a^2x^2}{n^2}}} \quad . \quad . \quad . \quad . \quad (17)$$

Sommerfeld then shows that in the case of a circular orbit the total energy W is given by

$$1 + \frac{\mathrm{W}}{m_0v^2} = \sqrt{1 - \frac{a^2x^2}{n^2}} \quad . \quad . \quad . \quad (18)$$

In the case of elliptical orbits the total quantum number n is resolved into the azimuthal quantum number k and the radial quantum number r, that is $n = r + k$. We have, however, already seen that owing to the advancing of the perihelion of the ellipse, k is now to be replaced by $k\gamma$, which from (12) is equal to $\sqrt{k^2 - a^2x^2}$. It follows therefore that the total energy in the case of elliptical orbits is given by

$$1 + \frac{\mathrm{W}}{m_0v^2} = \left[1 + \frac{a^2x^2}{(r + \sqrt{k^2 - a^2x^2})^2}\right]^{-\frac{1}{2}}$$

or

$$m_0v^2 + \mathrm{W} = m_0v^2\left[1 + \frac{a^2x^2}{(r + \sqrt{k^2 - a^2x^2})^2}\right]^{-\frac{1}{2}} \quad . \quad (19)$$

In order to find the effect of (19) when we consider the radiation of energy in passing from the initial state to the final state, we have from Bohr's equation

$$h\nu = \mathrm{W}_2 - \mathrm{W}_1 \quad . \quad . \quad . \quad . \quad (20)$$

where W_2 is the total energy of the initial orbit and W_1 that of the final orbit. If now in (19) we express the azimuthal and radial quantum numbers of the initial orbit by k_1 and r_1, and those of the final orbit by k and r, we have from (19) and (20)

$$\nu = \frac{m_0v^2}{h}\left[1 + \frac{a^2x^2}{(r_1 + \sqrt{k_1^2 - a^2x^2})^2}\right]^{-\frac{1}{2}} - \frac{m_0v^2}{h}\left[1 + \frac{a^2x^2}{(r + \sqrt{k^2 - a^2x^2})^2}\right]^{-\frac{1}{2}} \quad (21)$$

Since $$\alpha = \frac{2\pi e^2}{hv} \quad \text{and} \quad \mathrm{N} = \frac{2\pi^2 m_0 e^4}{h^3}$$ [1]

we have $$\frac{m_0 v^2}{h} = \frac{2\mathrm{N}}{a^2},$$

and consequently we can write (21) in the form

$$\nu = \frac{2\mathrm{N}}{a^2}\left\{\left[1 + \frac{a^2x^2}{(r_1 + \sqrt{k_1^2 - a^2x^2})^2}\right]^{-\frac{1}{2}} - \left[1 + \frac{a^2x^2}{(r + \sqrt{k^2 - a^2x^2})^2}\right]^{-\frac{1}{2}}\right\} \tag{22}$$

In the case of hydrogen, $x = \frac{\mathrm{E}}{e} = 1$, and therefore (22) is simplified to

$$\nu = \frac{2\mathrm{N}}{a^2}\left\{\left[1 + \frac{a^2}{(r_1 + \sqrt{k_1^2 - a^2})^2}\right]^{-\frac{1}{2}} - \left[1 + \frac{a^2}{(r + \sqrt{k^2 - a^2})^2}\right]^{-\frac{1}{2}}\right\} \tag{23}$$

This formula (23), as Sommerfeld says, includes all the spectroscopic phenomena which the hydrogen atom is capable of exhibiting.

In order to render the formula (22) convenient for purposes of calculation, Sommerfeld develops it in powers of the small quantity a^2. In cases, such as those of hydrogen and helium, where x is not greater than 2, it is sufficient to retain the first two powers of a^2 for visible and ultra-violet spectra, and these two cases we may deal with first. The required approximation is carried out as follows. We may denote the quantum sum which occurs in the denominator of (22) by S, and then

$$\mathrm{S} = r + \sqrt{k^2 - a^2x^2} = r + k - \frac{a^2x^2}{2k} + \ldots \tag{24}$$

Further, we have

$$\left[1 + \frac{a^2x^2}{\mathrm{S}^2}\right]^{-\frac{1}{2}} = 1 - \tfrac{1}{2} \cdot \frac{a^2x^2}{\mathrm{S}^2} + \tfrac{3}{8} \cdot \frac{a^4x^4}{\mathrm{S}^4} - \ldots \tag{25}$$

To the required degree of approximation we may put

$$\left.\begin{aligned} &\frac{1}{\mathrm{S}^2} = \left[r + k - \frac{a^2x^2}{2k}\right]^{-2} = \frac{1}{(r+k)^2}\left[1 + \frac{a^2x^2}{k(r+k)} + \ldots\right] \\ &\text{and} \\ &\frac{1}{\mathrm{S}^4} = \frac{1}{(r+k)^4}[1 + \ldots] \end{aligned}\right\} \tag{26}$$

[1] This is the Bohr value of N (see p. 65).

If we substitute these values in (25) we have

$$\left[1 + \frac{\alpha^2 x^2}{S^2}\right]^{-\frac{1}{2}} = 1 - \tfrac{1}{2} \cdot \frac{\alpha^2 x^2}{(r+k)^2} - \tfrac{1}{2} \cdot \frac{\alpha^4 x^4}{k(r+k)^3} + \tfrac{3}{8} \cdot \frac{\alpha^4 x^4}{(r+k)^4}$$

$$= 1 - \tfrac{1}{2} \cdot \frac{\alpha^2 x^2}{(r+k)^2} - \tfrac{1}{8} \cdot \frac{\alpha^4 x^4 (r+k)}{k(r+k)^4} + \tfrac{3}{8} \cdot \frac{k\alpha^4 x^4}{k(r+k)^4}$$

$$= 1 - \tfrac{1}{2} \cdot \frac{\alpha^2 x^2}{(r+k)^2} - \tfrac{1}{2} \cdot \frac{\alpha^4 x^4}{(r+k)^4}\left(\tfrac{1}{4} + \frac{r}{k}\right) \quad . \quad . \quad (27)$$

This development may now be inserted in (22) which contains the quantum numbers r_1, k_1 of the initial orbit, and the quantum numbers r, k of the final orbit. In taking the difference between the two terms in the square brackets, the first term, which is 1, cancels out and the factor $\frac{2}{\alpha^2}$ may be divided out. The wave-number ν is then given by the difference of a first positive member, depending on the quantum numbers k and r, and of a second negative member depending on the quantum numbers k_1 and r_1. This may be indicated by

$$\nu = (k, r) - (k_1, r_1) \quad . \quad . \quad . \quad . \quad (28)$$

For the first term in (28) we have

$$\frac{Nx^2}{(r+k)^2} + \frac{N\alpha^2 x^4}{4(r+k)^4} + \frac{N\alpha^2 x^4}{(r+k)^4} \cdot \frac{r}{k} + \quad . \quad . \quad (29)$$

and for the second term in (28)

$$\frac{Nx^2}{(r_1+k_1)^2} + \frac{N\alpha^2 x^4}{4(r_1+k_1)^2} + \frac{N\alpha^2 x^4}{(r_1+k_1)^4} \cdot \frac{r}{k} + \quad . \quad . \quad (30)$$

The observed wave-number ν of the radiations emitted when the electron falls from the orbit defined by the quantum numbers k_1, r_1 to the orbit defined by the quantum numbers k, r, will be given by the difference (29) — (30). Each of the two formulæ has three terms and consequently we may write

$$\nu = \nu_1 + \nu_2 + \nu_3,$$

where ν_1 is the difference between the two first terms, ν_2 the difference between the two second terms, and ν_3 that between the two third terms. We have therefore

$$\nu_1 = Nx^2\left[\frac{1}{(r+k)^2} - \frac{1}{(r_1+k_1)^2}\right] \quad . \quad . \quad (31)$$

which is identical with the formula (8) given on p. 107 for an elliptical orbit, and, indeed, is identical with the Bohr equation, since the sum of the azimuthal and radial quantum numbers equals the Bohr quantum number.

The second term difference is

$$\nu_2 = \frac{N\alpha^2 x^4}{4}\left[\frac{1}{(r+k)^4} - \frac{1}{(r_1+k_1)^4}\right] \quad . \quad . \quad (32)$$

and this gives a general increase in the wave-number which is the same for circular and elliptical orbits. It may be called the general relativity correction.

The third term difference is

$$\nu_3 = N\alpha^2 x^4\left[\frac{1}{(r+k)^4}\cdot\frac{r}{k} - \frac{1}{(r_1+k_1)^4}\cdot\frac{r_1}{k_1}\right] \quad . \quad . \quad (33)$$

and from this it can be seen that relativity brings about a separate increase in the wave-number for the various elliptical orbits. This increase depends on k and r individually and increases with the eccentricity of the orbit. Each emission, therefore, instead of being truly monochromatic, will depend on the ratios of the integers r/k and r_1/k_1.

We may now consider the application of these theoretical results to hydrogen in order to determine, in particular, the effect of the term ν_3. For this purpose we may take the first line of the Balmer series, the wave-number of which, as previously shown, is given by

$$\nu = 109678{\cdot}3\left(\frac{1}{2^2} - \frac{1}{3^2}\right),$$

where 2 and 3 are the Bohr quantum numbers for the final and initial orbits. The formula derived above, on p. 107, for elliptical orbits substitutes for the Bohr quantum numbers the sums of the azimuthal and radial quantum numbers, so that for this line $k + r = 2$ and $k_1 + r_1 = 3$. No alteration in the wave-number is caused thereby, and consequently we have from (31), since $x = \frac{E}{e} = 1$,

$$\begin{aligned}\nu_1 &= 109678{\cdot}3\left(\frac{1}{2^2} - \frac{1}{3^2}\right)\\ &= 15233{\cdot}10\\ \text{or } \lambda_{air} &= 6562{\cdot}845 \text{ A.}\end{aligned}$$

For the general relativity correction we have from (32)

$$\nu_2 = \frac{109678{\cdot}3\alpha^2}{4}\left(\frac{1}{2^4} - \frac{1}{3^4}\right),$$

where $\alpha^2 = 4\pi^2 e^4/h^2 v^2 = 5{\cdot}307 \times 10^{-5}$, using the values given for e, h, and v on p. 65. The value of ν_2 is therefore

$$\nu_2 = \frac{5{\cdot}834}{4}\left(\frac{1}{2^4} - \frac{1}{3^4}\right) = 0{\cdot}09.$$

The wave-number of the line corrected for the general relativity effect is

$$\nu_1 + \nu_2 = 15233{\cdot}19$$

or

$$\lambda_{\text{air}} = 6562{\cdot}806 \text{ A.}$$

The result of the third term is of very great interest and importance. In this term we have the two quantum number ratios r/k and r_1/k_1, and since $k + r = 2$ the ratio r/k has the value of either 0/2 or 1/1. Similarly, since $k_1 + r_1 = 3$, the ratio r_1/k_1 has the value of 0/3, 1/2, or 2/1.

If the two ratios be 0/2 and 0/3 respectively, it is obvious that the value of the term will be zero, and consequently a line will be obtained with the wave-number

$$\nu_1 + \nu_2 = 15233{\cdot}19.$$

If the two ratios be 1/1 and 0/3 respectively, then the value of the third term will be

$$\nu_3 = 5{\cdot}834\left(\frac{1}{2^4} - 0\right)$$

$$= 0{\cdot}3646.$$

There will, therefore, be a second line having the wave-number

$$\nu_1 + \nu_2 + \nu_3 = 15233{\cdot}5546.$$

It follows from this that the hydrogen line H_α will be double, the two principal components being separated by the interval

$$\Delta\nu = 0{\cdot}3646$$

or

$$\Delta\lambda = \frac{0{\cdot}3646}{\nu^2} = 0{\cdot}1571.$$

We have, however, still to take into account the ratio r_1/k_1 which may have the value of either 1/2 or 2/1, so that each line of the doublet will have two satellites. For the purposes of calculation it is more convenient to calculate the differences in wave-number between each component of the doublet and its two satellites. These are

$$\Delta\nu_a = 5{\cdot}834\left(\frac{1}{3^4} \times \frac{1}{2}\right) = 0{\cdot}0360$$

or

$$\Delta\lambda_a = 0{\cdot}0155,$$

and

$$\Delta\nu_b = 5{\cdot}834\left(\frac{1}{3^4} \times \frac{2}{1}\right) = 0{\cdot}1440$$

or

$$\Delta\lambda_b = 0{\cdot}0621.$$

It must be noted that the second term within the brackets of formula (33) is negative, and consequently the two satellites will have smaller frequencies than the two lines which they accompany, that is to say, they will be situated on the red side of the two components of the doublet.

The most important interval is the wave-number difference between the two principal components, and this may be written as $\Delta\nu_H$ the theoretical value for which is the same for all lines of the Balmer series, since in the case of all these lines $k + r = 2$. The values of $\Delta\nu_b = 4\Delta\nu_a$ and the wave-number differences between the lines in each triplet of H_a measured consecutively from the principal line are 0·0360 and 0·1080, and as may be seen from the formula (33) are $\frac{8}{81}\Delta\nu_H$ and $\frac{8}{27}\Delta\nu_H$, respectively.

In the case of H_β line for which $k_1 + r_1 = 4$ there will be two components ($\Delta\nu = 0{\cdot}3646$, $\Delta\lambda = 0{\cdot}0862$) and each of these will have three satellites associated with it, that is to say, the fine structure will consist of two quartets, each having identical separations between its components. In general, the number of satellites associated with each principal component of the doublet will be given by $r_1 + k_1 - 1$.

We may now consider the experimental evidence and see whether the very definite results obtained from the theory are confirmed by observation. As already stated at the beginning of this section, it has long been known that the hydrogen lines of the Balmer series are doublets and that the interval between them decreases with decreasing wave-length. This was first observed by Michelson (see Vol. II., Chap. I., p. 9), and has since been confirmed by several later observers. This gives a qualitative verification of the theory, and it may be pointed out in passing that the double nature of the lines of the Balmer series, previous to Sommerfeld's theory, was somewhat of a mystery. When the hydrogen lines are examined under very high resolving power, they exhibit a fine structure it is true, but the number of the components is not as great as that calculated from the formula (33). This is due to the principle of selection which, as we have already seen, states that when no external field is present, the transitions of the azimuthal quantum number are limited to ± 1, no restrictions being imposed on the transitions of the radial quantum number. In other words, the principle only allows those transitions for which $k_1 - k = \pm 1$, and consequently when no external field is present some of the lines of the total number rendered possible by the formula (33) do not appear. The effect of this is shown in Fig. 25, where I. and II. represent the two groups of principal lines and satellites, and *a*, *b*, *c* represent the principal line and the two satellites within each group.

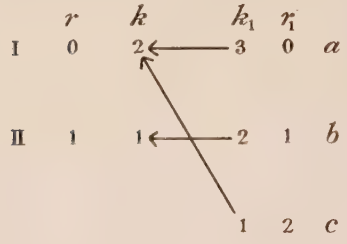


Fig. 25.

The arrows show the only transitions of the azimuthal quantum number which are allowed by the condition that $k_1 - k$ must equal ± 1. The transitions II.*a*, II.*c*, I.*b* are forbidden since k_1 would either jump by two units or remain the same. Consequently in the absence of

any external field the only components present will be I.*a*, I.*c*, and II.*b*. If the principle of selection be applied to the other lines of the Balmer series it will be found that the number of components in the absence of any external field will be limited to three in each case.

It follows from the principle of selection that the observed value of $\Delta\nu$ for the Balmer series will be somewhat smaller than the calculated value $\Delta\nu_H$. For example, in H_α the principal component I*a* is missing, with the result that the distance between the optical centres of gravity of the two ideal triplets will appear smaller than the theory leads us to expect. This agrees with observation since the mean of the values of $\Delta\nu$ for H_α obtained by several observers is 0·279, $\Delta\nu_H$ being 0·3645.

On the other hand, the principle of selection is invalidated when an external field is present and the theoretical number of components will appear. It is known that in the Stark effect,[1] that is under the influence of an external electric field, the number of visible components increases with the order number of the line in the Balmer series, which gives a second qualitative verification of the theory. Again, the theoretical number of components is obtained with a very strong current density as the first indication of an incipient Stark effect.

For the first quantitative proof of the theory we are indebted to Paschen[2] who succeeded in determining the value of $\Delta\nu_H$ from measurements of the fine structure of ionised helium lines, for which, as previously shown, $x = 2$. There is considerable advantage in testing the theory on helium, for the helium lines are sharper than those of hydrogen. They are less broadened by the Doppler effect due to heat motion, owing to the fact that the atom is four times as heavy as the hydrogen atom. Further, in the spectrum of He^+ the nucleus is doubly charged and the spectrum is less influenced by the Stark effect. In spite of this, the measurements require a resolving power that is very difficult to obtain. Although Paschen succeeded in measuring the fine structure of many helium lines, we may restrict ourselves to his measurements of the fine structure of the line $\lambda = 4687$, for these have the greatest probable accuracy. The formula for this line, omitting all relativity refinements, is

$$\nu = 4N\left(\frac{1}{3^2} - \frac{1}{4^2}\right),$$

and, since $k + r = 3$ and $k_1 + r_1 = 4$, the theoretical structure of the line consists of three quartets. Using a heavy spark discharge, Paschen observed nine out of the twelve lines and measured eight intervals. Two of these were also measured with a less heavy discharge. In Table CXIII. are given the results of Paschen's measurements, the first column containing the two components, the difference of whose wave-length, $\Delta\lambda$, is given in the second column. The third column

[1] The Stark effect will be described in Chapter III.
[2] *Ann. der Phys.*, **50**, 901 (1916).

contains the theoretical wave-length differences expressed as multiples of the standard value $\Delta\lambda_{He}$ for the line $\lambda = 4687$, and in the fourth column are given the values of $\Delta\lambda_{He}$ calculated from the observed values of $\Delta\lambda$. The fifth column contains the relative weight which Paschen assigns to each measurement.

TABLE CXIII.

	$\Delta\lambda$.		$\Delta\lambda_{He}$ (obs.).		
III.*a*-III.*c*	0·0906	$\Delta\lambda_{He}$	0·09060	0	
III.*a*-III.*d*	0·2418	$3\Delta\lambda_{He}$	0·08060	2	
III.*a*- II.*a*	0·3805	$3 \times 1{\cdot}5802\Delta\lambda_{He}$	0·08027	3	
III.*a*- I.*a*	0·5011	$4 \times 1{\cdot}5802\Delta\lambda_{He}$	0·07926	5	Strong spark discharge.
II.*a*- II.*b*	0·0296	$\frac{1}{3}\Delta\lambda_{He}$	0·0888	0	
II.*a*- II.*c*	0·0867	$\Delta\lambda_{He}$	0·0867	0	
II.*a*- II.*d*	0·2385	$3\Delta\lambda_{He}$	0·0795	2	
I.*a*- I.*d*	0·2417	$3\Delta\lambda_{He}$	0·08057	2	
III.*a*-III.*c*	0·0811	$\Delta\lambda_{He}$	0·0811	1	Spark discharge and continuous current.
III.*a*-III.*d*	0·2426	$3\Delta\lambda_{He}$	0·08087	2	

The mean value of $\Delta\lambda_{He}$ obtained from the values given in the fourth column is 0·08007 ± 0·0010 Ångström, and from this the value of the standard hydrogen wave-number interval $\Delta\nu_H = 0{\cdot}08007/(4687)^2 = 0{\cdot}3645 \pm 0{\cdot}0045$. This value is extraordinarily close to the theoretical value given above, 0·3646.

More recently the value of $\Delta\nu_H$ has been directly measured by Shrum [1] in Toronto, who employed a vacuum tube cooled by means of liquid air. The measurements are given in Table CXIV.

TABLE CXIV.

	λ.	$\Delta\lambda$.	$\Delta\nu_H$.	Probable error.
H_α	6562·793	0·143A.	0·33	± 0·02
H_β	4861·327	0·085	0·36	± 0·01
H_γ	4340·466	0·070	0·37	± 0·02
H_δ	4101·738	0·061	0·36	± 0·02
H_ϵ	3970·075	0·055	0·35	± 0·02

Although these measurements are not of the same accuracy as those of Paschen, this confirmation of the value of $\Delta\nu_H$ by direct measurement is of great interest.

There thus can be no doubt that the relativity equation (33) has found complete verification in experimental observation, and that the general theory of atomic phenomena has been placed on an entirely firm basis. As Sommerfeld says, the absolute theory has come to grief owing to spectroscopic facts and has to give up to the theory of relativity the position of sovereignty which it formerly held.

There still remains the question of the relative intensities of the

[1] McLennan, *Nature*, **112**, 166 (1923).

various components, and there appears to be no straightforward expression which gives these intensities. Sommerfeld assumed that in any doublet the intensities will decrease in the ratio 2 : 1, in a triplet 3 : 2 : 1, in a quartet 4 : 3 : 2 : 1, in the order of the circular orbit to the increasingly eccentric orbits. In the H_α line the intensities of the components of the first triplet I.*a* I.*b*, I.*c* will be 6/6, 4/6, 3/6, and in the second triplet 3/6, 2/6, 1/6 respectively. In the absence of any external electric field, as shown above, I.*b*, II.*a*, and II.*c* are not present. This distribution of intensities, however, has been definitely proved by observation to be incorrect, and the question has been discussed in a very important paper by Kramers.[1] From the point of view of the validity of Sommerfeld's theory, the question is perhaps of secondary importance, but it comes into great prominence when the optical centre of gravity of the components of the hydrogen doublet or helium triplet are measured. The whole question has been well discussed by Birge,[2] who shows that the breadth of the components of H_α and H_β and the intervals between them should be the same as those observed by Merton.[3]

X-Ray Spectra.—The relativity formula (22) on p. 246 has also been applied by Sommerfeld to the doublets in the X-ray region. Most valuable and important work has been carried out by Millikan and Bowen, in which they have linked up these doublets with ordinary spectral series, but in order to enable us to understand the significance of this it is necessary first to discuss the salient features of X-ray spectra and their relativistic treatment.

This account must of necessity be restricted in a chapter which claims only to deal with spectral series, but it must not be forgotten that X-ray spectra have proved to be of immense value in connection with the general problem of atomic structure. As is well known, investigations in the field of X-rays have followed two very distinct lines; in the one the characteristic X-ray spectra of the elements form the subject of study, and in the other the structure of crystals is finding elucidation by the utilisation of X-rays of known wave-length. This arises from the initial discovery by Laue [4] that just as a grating is adapted to the diffraction of ordinary light and determination of wave-length, so is the structure of crystals adapted to the very short wave-length of X-rays. The experimental methods employed in these two fields of work cannot be given here, and, indeed, we can only consider the quantitative relations between the wave-lengths of the characteristic lines of the X-ray spectra of the elements.[5]

[1] *D. Kgl. Danske Vid. Selsk. Skr. natur og math. Afd.*, 8, III., 3 (1919).
[2] *Phys. Rev.*, **17**, 589 (1921). [3] *Proc. Roy. Soc.*, A, **97**, 307 (1920).
[4] See *Jahrb. für Radioaktivität und Elektronik*, **11**, 308 (1914).
[5] Professor Sommerfeld gives in his book, *Atombau und Spektrallinien*, 4th Edition, Chapters 4 and 6, a full account of X-ray spectra of the elements. Crystal structure is dealt with by Sir William Bragg in *X-rays and Crystal Structure* (Bell & Sons, London, 1916); and by P. P. Ewald, *Kristalle und Rontgenstrahlen* (Springer, Berlin, 1923).

In discussing X-ray spectra, which are those given when the electrons are displaced from the innermost shells of electrons, we find that the quantitative relations are simpler than in the case of ordinary spectra, which are due to the outermost electrons. The explanation of this is to be found in the fact that the inner electrons come under the influence of the nuclear charge far more than do those in the periphery of the atom, and in consequence they obey simpler laws.

At the commencement it will be advisable to devote a few lines to the system of nomenclature which had its origin in the days before the nature of X-rays was understood. The essential characteristic of these rays as shown by Röntgen when he first discovered them in 1895 was their remarkable penetrative power towards a sheet of aluminium. Barkla, to whose early pioneer work much is due, proved that when cathode rays or X-rays fall on an element, it emits characteristic rays of a definite hardness. This hardness was measured by the penetrative power those characteristic rays have towards a sheet of some material such as aluminium. He further showed that the absorptive power of the aluminium obeyed very simple laws, and concluded from this that the radiation must be very nearly homogeneous. The hardness, therefore, at that time was defined as penetrative power. Barkla further showed that a simple relation exists between the hardness of the characteristic X-rays and the atomic weight of the element which emits them. With increase in the atomic weight of the element, the hardness increases, and he concluded that the characteristic X-ray radiation is a property of the elementary atom and is determined by the atomic weight.

In addition to this, Barkla demonstrated that a single element can give two different characteristic X-ray radiations, one of which is much harder than the other. The harder type he called the K radiation and the softer type he called the L radiation, and these designations are still used. An important point was noted by Barkla in that the radiation which excites the characteristic radiation must be harder than the latter. For this reason he looked on the characteristic radiation as fluorescent light, thereby finding an analogy with the Stokes rule in fluorescence emission spectra. If the characteristic radiation is excited by X-rays then these must be harder than those emitted, and if it is excited by cathode rays these must travel with a velocity which exceeds a critical limit.

As the result of Laue's discovery, the hardness of X-rays was replaced by quantitative measurements of wave-length and great advances were quickly made. The K and L radiations were found to be line spectra of a simple type, and we now speak of the K series and the L series of lines. Then, owing to the brilliant work of Moseley, it was found that there exists a simple numerical relation between the wave-length of the X-ray spectra lines and the atomic number of the element producing them. Further, Siegbahn found that yet another series of lines exist, the wave-lengths of which are larger than those of the K and L series, and to these he gave the name of M rays.

The K series of lines arise from the displacement of an electron from the innermost shell of electrons, and, since the influence of the nucleus is the greatest, the K series of lines has the smallest wave-lengths corresponding to the greatest amounts of energy involved in the transitions which give rise to them. Next in order come the displacements from the L, M, N, etc., shells, with increase in the wave-lengths of the characteristic lines. Table CXII., on p. 241, shows how with increasing atomic number the K, L, and M, etc., shells are progressively built up.

When an electron is removed from the K shell and displaced to the periphery of the atom, the tendency is at once for the K shell to be reconstituted.[1] This may be achieved by the transference of an electron to the K shell from either the L shell, M shell, or some other shell. The energy radiated depends, of course, on the shell from which this electron starts, being the greater the more distant the starting-point is from the K shell. The spectrum line emitted when the electron passes from the L shell to the K shell is known as the K_α line, the K_β and K_γ lines being given by the transitions from the M and N shells respectively. It thus follows that the K_α, K_β, and K_γ lines are in decreasing order of wave-length. If we take into account the relative probabilities of these three possible transitions we can arrange them in decreasing order, namely $L \rightarrow K$, $M \rightarrow K$, and $N \rightarrow K$. It thus follows that the lines K_α, K_β, K_γ will be in decreasing order of intensity, as is indeed the case. All the lines which are due to transitions having the K shell as their end point belong to the K series, whilst all those due to transitions to the L and M shells are known as the L series and M series respectively.

We may first consider the K series of lines which formed the subject of Moseley's investigation and led him to the great discovery of the numerical relationship already referred to.[2] He examined the characteristic K spectra emitted by calcium, titanium, vanadium, chromium, manganese, iron, cobalt, and nickel, and found that the spectrum consisted in each case of two lines which were the K_α and K_β lines. The resolving power was not sufficient to show the K_γ line separated from the K_β line. Moseley noted that the X-ray spectrum is a definite characteristic of the atom and is, moreover, an additive property since the X-ray spectrum of brass shows the K lines of copper and zinc with their correct wave-lengths.

He showed that the frequencies of the lines increase with the atomic weight and, further, that the frequencies are proportional to

$$A(Z - s)^2$$

where A and s are constants, and Z is the atomic number. Apart from its fundamental importance as regards atomic physics, this discovery was of singular interest to chemists, since it threw a new light on the periodic classification of the elements. It is now a matter

[1] Kossel, *Deutsch. phys. Ges. Verh.*, **16**, 899, 953 (1914); **18**, 339 (1916).
[2] *Phil. Mag.*, **26**, 1024 (1913); **27**, 703 (1914).

of history that the old arrangement of the elements in ascending order of atomic weights gave immediate place to their arrangement by atomic numbers, and that in this way the anomalous positions of argon and potassium, tellurium and iodine, cobalt and nickel found their true explanation. Furthermore, the vacant places in the periodic system became at once clear and defined.

Turning once again to the K series it has been found that there are present more lines than the three already mentioned, owing to the fact that the L, M, N, etc., shells contain more than one level in each case. Altogether in elements of very high atomic number such as thorium where the P shell comes into play there are ten possible transitions giving rise to ten lines in the K series. For a full account of the various possible combinations in the K, L, and M series reference may be made to Sommerfeld's book. For our present purpose, namely, an introduction to Millikan's work, the elementary facts need only be considered. The four most important K lines are those which arise from transitions from two L levels and two M levels, and these may be called the K_α, $K_{\alpha'}$, K_β, and $K_{\beta'}$ lines respectively. The most convenient method of expressing the linear relations found by Moseley is to plot the values of $\sqrt{\frac{\nu}{N}}$ against the atomic number, where N is the Rydberg constant. If ν is expressed in wave-numbers, the difference between the values of $\sqrt{\frac{\nu}{N}}$ for the K_α lines of two consecutive elements is about 0·866. Now 0·866 is equal to $\sqrt{3/4}$, and consequently for the K_α line we may express the Moseley relation by

$$\frac{\nu}{N} = \tfrac{3}{4}(Z - s)^2.$$

But s is almost equal to unity, and we have, therefore,

$$\frac{\nu}{N} = \tfrac{3}{4}(Z - 1)^2 = (Z - 1)^2\left(\frac{1}{1^2} - \frac{1}{2^2}\right).$$

This expression exhibits a remarkable analogy with the formula for the Balmer series of hydrogen lines. In its most general form this formula is

$$\nu = N\left(\frac{E}{e}\right)^2\left(\frac{1}{n^2} - \frac{1}{n_1^2}\right)$$

and since $E = Ze$

$$\nu = NZ^2\left(\frac{1}{n^2} - \frac{1}{n_1^2}\right).$$

Thus the only difference is that in the K series the full value of Z does not come into play but it is reduced by the constant s, which, in the case of the K_α line, is equal to unity. Sommerfeld calls this constant the screening constant.

It must be noted that the linear relation between $\sqrt{\frac{\nu}{N}}$ and Z is not absolute, since the line exhibits a slight curvature. The Moseley relation can, indeed, no longer be considered as exact. The true expression is attained by the application of a relativity correction. Again, since the lines are due to electron transitions, their frequencies must be given by the difference between two terms, just as in ordinary spectral series.

In order to displace an electron from the K, L, and M shells to the periphery of the atom definite quantities of energy will be required. If these three quantities of energy, divided by the Planck constant h, be denoted by K, L, and M, then we have

$$K_\alpha = K - L \qquad K_\beta = K - M \qquad K_\gamma = K - N$$
$$L_\alpha = L - M \qquad L_\gamma = L - N$$
$$M_\alpha = M - N$$

It follows from this, as pointed out by Kossel, that

$$K_\beta = K_\alpha + L_\alpha, \quad K_\gamma = K_\alpha + L_\gamma, \quad K_\gamma = K_\beta + M_\alpha, \quad L_\gamma = L_\alpha + M_\alpha,$$

if the symbols for the lines represent their frequencies. If their wave-numbers are used the energy quantities necessary for the electron displacement must, of course, be divided by hv, where v is the velocity of light.

Since the K_α line is due to the combination of two terms, the Moseley relation cannot be exact unless the screening-constant, s, be the same for the two terms. This cannot be assumed, it being more probable that it is smaller for the K term than for the L term. "In spite of this," as Sommerfeld says, "it will always be noteworthy that Moseley, in his first entry into the realm of quantitative X-ray spectroscopy, made the first and most important step in the theoretical explanation of high frequency spectra."

The L series has a more complex structure than the K series, owing to the greater number of the levels involved. The important feature of this series from our present standpoint is the existence of doublets. There are two types, namely, the L doublets, which are due to transitions from the same initial level (M, N, or O level) to two L levels, and the M doublets of the L series, which are due to transitions from two different M levels to the same L level. These doublets exhibit a remarkable feature in that each doublet series has a wave-length difference which is nearly constant throughout the whole series of elements. This constancy is particularly evidenced in the M doublets of the L series, the tendency in the L doublets being for the value $\Delta\lambda$ to decrease slightly with increase in atomic number.

If, as in the case of the K series, the values of $\sqrt{\frac{\nu}{N}}$ be plotted for the L series against the atomic number, the relation between the two

is found to be approximately linear. The lines show a slight curvature which is due to the want of the relativity correction. The relation, however, is not so simple as it is in the case of the K series, since some of the lines obtained on plotting the values for the different members of the L series cross one another.

If now the values of $\Delta\nu/N$ are compared for all the L doublets it is found that, within the limits of experimental error, these are constant for any one element. Further than this, it is found that the values of $\sqrt[4]{\Delta\nu/N}$ form an arithmetical progression, that is to say, there is a linear relation between $\sqrt[4]{\Delta\nu/N}$ and the atomic number.

The foregoing relations can be expressed in the following way.[1] The separation of the doublets in wave-numbers is

$$\Delta\nu = \frac{1}{\lambda_1} - \frac{1}{\lambda_2} = \frac{\Delta\lambda}{\lambda_1\lambda_2} = \frac{\Delta\lambda}{\lambda^2} = \Delta\lambda\nu^2,$$

if λ and ν be the mean wave-length and wave-number, respectively, of the doublet. We have already seen that for any one series of doublets $\Delta\lambda$ is a constant and is independent of the atomic number, and if we put $\Delta\lambda = a^4$ we have $\sqrt[4]{\Delta\nu} = a\sqrt{\nu}$. It has been shown that $\sqrt[4]{\Delta\nu}$ is a linear function of the atomic number, and the same is true of $a\sqrt{\nu}$ by Moseley's law, not only for the lines of the K series, but also for those of the L and M series. Now the value of $\sqrt[4]{\Delta\nu/N}$ for the L doublet increases by 0·043 when the atomic number increases by unity, the relation between the two being given by

$$\sqrt[4]{\frac{\Delta\nu}{N}} = 0{\cdot}043(Z - 3{\cdot}5),$$

This can be written in the form

$$\frac{\Delta\nu}{N} = \frac{5{\cdot}3 \times 10^{-5}}{2^4}(Z - 3{\cdot}5)^4.$$

This law is of great importance in connection with the inner structure of atoms; it leads us not only to the rules of the quantum theory which hold for the inner structure, but also to the laws of the relativity theory. The law was derived for the L doublets, but it also holds good for all analogous doublets. In the M doublets the value 2^4 in the denominator is replaced by 2×3^4 and the constant 3·5 has a different value.

We may now consider in a very brief way the application of the relativistic principle to the X-ray doublets of the L, M, and N series. In order to understand the phenomena it is necessary to assign symbols to the various levels to which these doublets are due, and we may use those adopted by Bohr. The L doublets are due to the L_{II} and

[1] Sommerfeld, *loc. cit.*, p. 278.

L_{III} levels, and similarly we have the M_{II}, M_{III}, and N_{II} and N_{III} levels. We may direct our attention in particular to the L doublets.

For the relativistic treatment of X-ray spectra we are indebted to Sommerfeld, who points out that from the minute relativity doublet of hydrogen a direct road proceeds through the fine structure lines of He^+ to the doublets of X-ray spectra. The relativity formula (22) on p. 246 was developed in a way suitable for application to the cases of H and He^+, but it is necessary for the purposes of X-ray spectra to carry the accuracy of the calculations further and retain still higher powers of α^2. Sommerfeld [1] does this and arrives at the following formula for the separation in wave-numbers of the L doublet

$$\Delta\nu_L = N\frac{\alpha^2x^4}{2^4}\left(1 + \frac{5}{2}\cdot\frac{\alpha^2x^2}{2^2} + \frac{53}{8}\cdot\frac{\alpha^4x^4}{2^4} + \ldots\right) \quad . \quad (1)$$

where, as before, $\alpha^2 = 5{\cdot}3 \times 10^{-5}$, $x = E/e$, and $N = N_\infty$.

This result means that the separation of the L doublet is fully determined and rationally expressed by α^2, N_∞, and x. As regards the last, it would seem at first sight that we should make x equal to the atomic number, that is to say, $x = Z$. On the other hand, the orbits of the two electrons in the K shell lie between the nucleus and the L orbits, and these must screen off the true nuclear charge. In addition, when the L shell is completely filled, its electrons must also screen off the nuclear charge. The result is that the true nuclear charge cannot be effective, but must be reduced by an amount which is dependent on this screening. We therefore have an effective charge which can be expressed by

$$x = Z - s,$$

and hence the name of screening constant is given to the term s. It is not possible to calculate the value of s from theory, and we can only arrive at it from observation. It may be pointed out, however, that in the simplest possible case, namely, Li I., where there is only one L electron screened by two K electrons, the value of s will be 2. This is important in view of Millikan and Bowen's work.

In order to obtain a general idea as to the value of s in X-ray spectra we may take the first term only of equation (1) and put

$$\Delta\nu_L = \frac{N\alpha^2}{2^4}(Z - s)^4 \quad . \quad . \quad . \quad . \quad (2)$$

This represents to a first approximation the theoretical value of $\Delta\nu_L$ deduced from hydrogen, or rather semi-theoretical value, since the parameter s has been introduced. This formula may be compared with the empirical formula derived above

$$\frac{\Delta\nu_L}{N} = \frac{5{\cdot}3 \times 10^{-5}}{2^4}(Z - s)^4,$$

[1] *Atombau und Spectrallinien*, 4th Edition, p. 442 *et seq.* Vieweg, Braunschweig, 1924.

and as can be seen the two agree not only in their general form but also in their numerical value.

We have already seen, on p. 249, that the separation of the hydrogen doublet is given by

$$\Delta\nu_{\mathrm{H}} = \frac{\mathrm{N}\alpha^2}{2^4} = 0{\cdot}365,$$

and we may therefore write (2) in the form

$$\Delta\nu_{\mathrm{L}} = \Delta\nu_{\mathrm{H}}(\mathrm{Z} - s)^4 = 0{\cdot}365(\mathrm{Z} - s)^4.$$

It may thus be seen that the L doublet is a gigantic magnification of the hydrogen doublet. For this reason these doublets are often called relativity or regular doublets, in order to differentiate from another set of doublets which will presently be considered.

The relativity formula not only is valid for the L doublets but also for the M and N doublets. If we use the Bohr nomenclature for the various orbits the values given by Sommerfeld for the separations are as follows :—

$$\mathrm{M_{II}M_{III}} \qquad \frac{\Delta\nu}{\mathrm{N}} = \frac{\alpha^2x^4}{3^4}\left(\frac{3}{2} + \frac{279}{32}\cdot\frac{\alpha^2x^2}{3^2} + \frac{13059}{256}\cdot\frac{\alpha^4x^4}{3^4} + \ldots\right)$$

whence $\Delta\nu = 0{\cdot}108(\mathrm{Z} - s)^4$;

$$\mathrm{M_{IV}M_{V}} \qquad \frac{\Delta\nu}{\mathrm{N}} = \frac{\alpha^2x^4}{3^4}\left(\frac{1}{2} + \frac{25}{32}\cdot\frac{\alpha^2x^2}{3^2} + \frac{317}{256}\cdot\frac{\alpha^4x^4}{3^4} + \ldots\right)$$

whence $\Delta\nu = 0{\cdot}0360(\mathrm{Z} - s)^4$;

$$\mathrm{N_{II}N_{III}} \qquad \frac{\Delta\nu}{\mathrm{N}} = \frac{\alpha^2x^4}{4^4}\left(2 + 20\frac{\alpha^2x^2}{4^2} + \frac{809}{4}\cdot\frac{\alpha^4x^4}{4^4} + \ldots\right)$$

whence $\Delta\nu = 0{\cdot}0456(\mathrm{Z} - s)^4$;

$$\mathrm{N_{IV}N_{V}} \qquad \frac{\Delta\nu}{\mathrm{N}} = \frac{\alpha^2x^4}{4^4}\left(\frac{2}{3} + \frac{56}{27}\cdot\frac{\alpha^2x^2}{4^2} + \frac{5905}{972}\cdot\frac{\alpha^4x^4}{4^4} + \ldots\right)$$

whence $\Delta\nu = 0{\cdot}0152(\mathrm{Z} - s)^4$;

$$\mathrm{N_{VI}N_{VII}} \qquad \frac{\Delta\nu}{\mathrm{N}} = \frac{\alpha^2x^4}{4^4}\left(\frac{1}{3} + \frac{23}{54}\cdot\frac{\alpha^2x^2}{4^2} + \frac{1069}{1944}\cdot\frac{\alpha^4x^4}{4^4} + \ldots\right)$$

whence $\Delta\nu = 0{\cdot}0076(\mathrm{Z} - s)^4$.

The values of $\Delta\nu$ are those given by the first term in each expression. It must, of course, be noted that the value of the screening constant is different for the L, M, and N shells, and, indeed, different for the different M and N doublets. Thus for the two M doublets $s = 8{\cdot}3$ and 13, respectively, and for the three N doublets $s = 17$, 25, and 34, respectively. This growth of the screening constant is satisfactory in that it points to an increase in the number of electrons interposed. As Sommerfeld says, this must not tempt us to believe that we can approach the question of screening, and indeed, of the constitution of the shells by means of elementary notions of atomic

models. In the first place, the marked differences in the screening constants within the same shell are inexplicable by means of the model. Still more important is the fact that if we wished to apply the values of s, experimentally determined, to the calculation of the terms themselves, we would arrive at an entirely inadequate agreement with experiment. It is quite true that the terms on the whole follow the Moseley relation, that is to say, relativity corrections apart, they show a quadratic relation with the atomic number, but a new value of the screening constant must be used, different from that in the corresponding doublet.

The wave-number value of a level n_k given by Sommerfeld is

$$\nu = Nx^2\left[\frac{1}{n^2} + \frac{\alpha^2 x^2}{n^4}\left(\frac{n}{k} - \frac{3}{4}\right) + \ldots\right]$$

and in order to take into account the foregoing he introduces into the first term a screening constant σ which differs from that in the term giving the relativity correction. We thus have

$$\frac{\nu}{N} = \frac{1}{n^2}(Z-\sigma)^2 + \frac{\alpha^2}{n^4}(Z-s)^4\left(\frac{n}{k} - \frac{3}{4}\right) + \ldots$$

In order to obtain the foregoing values of $\Delta\nu/N$ for the relativity doublets by the difference of the two terms it is only necessary to give the constant σ and the constant s the same value for the two terms of a relativity doublet.

We have now to consider the irregular doublets which in the case of the L series are due to the fact that there are three L levels, namely, L_I, L_{II}, and L_{III}, these doublets being due to the difference L_I L_{III}. These irregular L doublets obey a law which was first enunciated by Hertz.[1] This law expressed graphically states that if, following Moseley, $\sqrt{\nu}$ is plotted against the atomic number Z, the graphs for L_I and L_{II} run parallel to one another, whilst the graphs for L_{II} and L_{III} diverge more and more from each other in accordance with the law for regular or relativity doublets. This means that $\sqrt{\nu_I} - \sqrt{\nu_{II}}$ is a constant. It was shown by Wentzel [2] that the same is true for the irregular doublets of the M and N series. If we express the wave-number ν of the individual limit approximately by the Moseley formula we have [3]

$$\frac{\nu}{N} = \frac{1}{n^2}(Z-\sigma)^2 \quad \text{or} \quad \sqrt{\frac{\nu}{N}} = \frac{Z-\sigma}{n}$$

where n is the total quantum number and σ is the screening constant which now comes into play. Just as the constant s in the case of the relativity doublets has two different values for the two levels

[1] *Zeitsch. für Phys.*, **3**, 19 (1920). [2] *Ibid.*, **6**, 84 (1921).
[3] Sommerfeld, *loc. cit.*, p. 456.

concerned, so we assume that the same is true for the constant σ. Then, if these two values be σ_1 and σ_2 we have

$$\Delta\sqrt{\frac{\nu}{N}} = \frac{\sigma_1 - \sigma_2}{n} = \frac{\Delta\sigma}{n},$$

remembering that n has the same value for two levels in the same shell. It follows, therefore, that

$$\frac{\Delta\nu}{N} = \frac{2\Delta\sigma}{n^2}\left(Z - \frac{\sigma_1 + \sigma_2}{2}\right).$$

The difference between irregular and regular doublets can be expressed in the following way. In the irregular doublets the separation increases linearly with the atomic number, whilst in the regular doublets it increases with the fourth power. Strictly speaking, the values of $\sqrt{\nu_I} - \sqrt{\nu_{II}}$ are not constant, owing to the influence of relativity terms which have not been taken into consideration. A more accurate statement of the Hertz law is that in the regular doublets the values of $\sigma_1 - \sigma_2$ are exactly constant, those of $\Delta\sqrt{\nu}$ being only approximately so.

The Spectra of Stripped Atoms.—We may now discuss the results obtained by Millikan and Bowen, and commence with the stage which was reached in 1921,[1] the complete measurements being published in 1924.[2] In this work, since the main object was identification of as many new lines as possible,[3] resolution was sacrificed to intensity, but, as will presently be seen, higher resolving power was subsequently employed. The key to the identification of the lines in the very short wave region was found in the discovery that in the region between $\lambda = 1000$ A. and 330 A. chemically pure magnesium and aluminium give spectra which are practically identical, whereas above $\lambda = 1300$ the lines are quite different and belong to the spectra of these two metals. The spectrum below $\lambda = 1000$ is the nearly pure spectrum of the oxygen atom, and this identification was checked by the fact that the spectrum appears practically complete with all oxidisable electrodes, becoming less intense as the electrodes become less and less oxidisable, and disappearing entirely with silver. The oxygen spectrum being known, and there being practically no aluminium lines between $\lambda = 1300$ and $\lambda = 230$, the spectrum of carbon was obtained in that region by eliminating from the observed carbon spectrum the oxygen and aluminium lines, since these were the only probable impurities. By the extension of this method the lines of the other elements examined were recognised.

In the case of lithium no lines were observed between $\lambda = 1700$ and $\lambda = 370$. This is a striking proof that great gaps exist between the K and L series in optical spectra as well as in X-ray spectra.

[1] *Proc. Nat. Acad. Sci.*, **7**, 289 (1921). [2] *Phys. Rev.*, **23**, 1 (1924).

[3] The excitation of these lines by means of hot sparks was described in vol. i., chap. viii., p. 273.

The K_α line of lithium should occur at λ = 240, but it was not observed at that time owing to the best gratings not being available. The valency electron of lithium is in an L ring with the result that the ordinary spectra of this element form the L series. If the brightest line be denoted by L_α, then the red line at λ = 6708 is the L_α line of lithium.

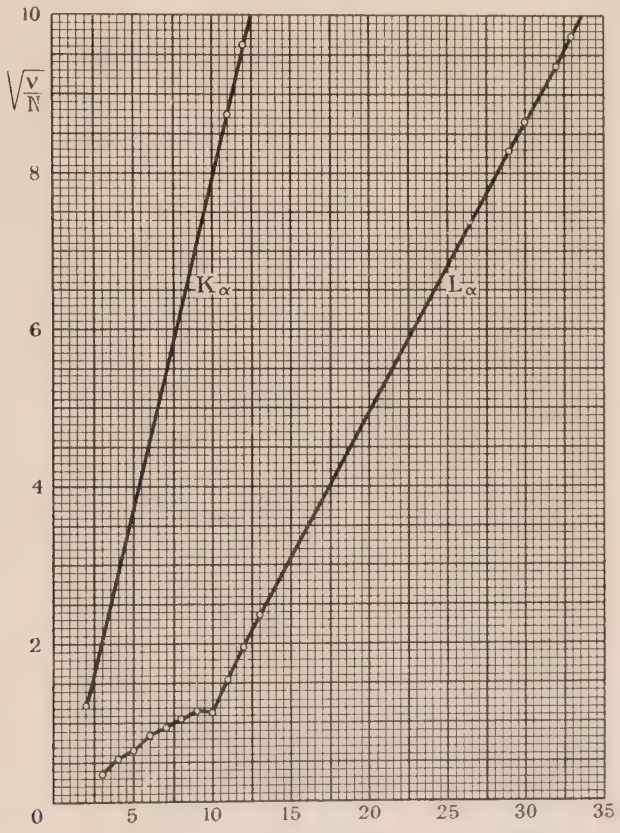


FIG. 26.

In Fig. 26 are shown the relations between the atomic numbers and the values of $\sqrt{\frac{\nu}{N}}$ for the L_α lines of the lighter elements investigated by Millikan and Bowen. The only value not directly observed is that of neon, which was calculated from the resonance potential of this gas. The K_α values have been inserted from the work of others.

The spectrum due to the two L electrons of beryllium begins on

the short wave side at $\lambda = 2175$ and reaches its maximum at the doublet at $\lambda = 3131{\cdot}2$ and $3130{\cdot}2$. This, then, may be taken as the L_α doublet, and is inserted in Fig. 26, together with the 6708 line of lithium.

The spectrum due to the three L electrons of boron begins at $\lambda = 676{\cdot}8$, and the strongest doublet, L_α, is that at $\lambda = 2497{\cdot}8$ and $2496{\cdot}9$. Since the K_α line is at $\lambda = 67{\cdot}2$, the ratio of the L_α to the K_α frequency is about 37.

The spectrum of carbon was obtained by the use of gas carbon electrodes which showed as their chief impurities oxygen, nitrogen, silicon, hydrogen, and aluminium, whilst traces of sodium, boron, and calcium also appeared. There are very many lines shown by carbon between $\lambda = 1833$ and $\lambda = 360{\cdot}5$. Those due to the four L electrons begin at $\lambda = 360{\cdot}5$ and reach their maximum intensity at $\lambda = 1335{\cdot}0$. This, therefore, is taken as the L_α line, and, since the K_α line is at $\lambda = 44{\cdot}4$, the ratio of K_α to L_α frequency in carbon is about 30.

The chief characteristics of the nitrogen spectrum were predicted before they were experimentally observed. On the one hand, there is the carbon L spectrum commencing at $\lambda = 360$ and reaching its maximum intensity at the L_α line $\lambda = 1335$. On the other hand, the oxygen spectrum begins at $\lambda = 140$ and reaches an unmistakable maximum at $\lambda = 834$, the L_α line. A general progression of spectra with atomic number towards higher and higher frequencies is unmistakable, but no nitrogen lines were known except those at $\lambda = 1494{\cdot}8$ and $1492{\cdot}8$ observed by Lyman. It was clear that the L_α line of nitrogen must lie between $\lambda = 1335$ and $\lambda = 894$, and on using ammonium nitrate fused into hollow aluminium electrodes a spectrum was obtained with a strong line at $\lambda = 1085{\cdot}2$. The only other strong lines observed were at $\lambda = 991{\cdot}1$, $916{\cdot}2$, and $685{\cdot}6$, the Lyman pair being relatively faint. Since the K_α line of nitrogen is at $\lambda = 31{\cdot}2$, the K_α/L_α ratio for nitrogen is 34·8.

The spectrum of fluorine was observed by the use of sodium fluoride fused into hollow aluminium electrodes. Only two strong lines were observed at $\lambda = 656{\cdot}4$ and 607, and the former being the stronger, was taken as the L_α line.

The sodium spectrum obtained with electrodes of pure sodium as well as with sodium fluoride shows only one unmistakable line in the whole region studied ($\lambda = 2000$ to $\lambda = 300$), namely, one at $\lambda = 372{\cdot}3$. There is a second line of less intensity at $\lambda = 376{\cdot}6$. As can be seen from Table CXII., on p. 241, the L shell of sodium is complete, the single valency electron being on an M level. This electron is in an energy level, the frequency value of which is represented by the limit of the principal series, $\nu_m = 41449{\cdot}0$ in wave-numbers. When an electron is removed from the L shell of sodium the M electron jumps into its place, the radiation emitted being the L_α line. By the Kossel relation given above on p. 257 the wave-number of the L_α line is given by

$$\nu = L - M$$

where L and M represent the wave-number values of the L and M levels. Now the wave-number of the 372 line is 268640 and the value of M in wave-numbers we have seen is 41449, and we thus have

$$\begin{aligned} L &= 268640 + 41449 \\ &= 310089. \end{aligned}$$

From this we find $L/N = 2{\cdot}8258$ and $\sqrt{L/N} = 1{\cdot}6810$. It is known from X-ray spectra that the L shell consists of three levels denoted by Bohr as L_I, L_{II}, and L_{III}, and by Sommerfeld as L_{22}, L_{21}, and L_{11}, respectively. The values of $\sqrt{\nu/N}$ for the L_{II} and L_{III} levels of aluminium, magnesium, sodium, and neon are 2·28, 1·87, 1·49, and 1·11, respectively,[1] and it is thus obvious that the observed line at $\lambda = 372{\cdot}3$ cannot correspond to the jump of the electron to either the L_{II} or the L_{III} level. The only remaining possibility is the jump to the L_I level, and in this way the value of this level is fixed at $\nu/N = 2{\cdot}8258$.

In the case of magnesium the spectrum only contains three lines of reasonable intensity at $\lambda = 323{\cdot}2$, 320·9, and 231·6, and the position of these lines indicates that they must belong to the L spectrum of magnesium. The M shell here contains two electrons, both moving in 3_1 orbits (see p. 241), and the only possible electron jumps are into the L_I, L_{II}, and L_{III} orbits. The last two should give the L doublet and the first should give a single line. We may first consider the transitions from the M_I orbit to the L_{II} and L_{III} orbits. The wave-number value of the 3_1 level is the limit of the principal series of singlets of magnesium, namely, $\nu = 61672{\cdot}1$. From the Kossel relation as applied to the two lines $\lambda = 323{\cdot}2$ ($\nu = 309380$) and $\lambda = 320{\cdot}9$ ($\nu = 311640$) we obtain the values $L_{II} = 373310$ and $L_{III} = 371050$. From these we have $L_{II}/N = 3{\cdot}4019$, $L_{III}/N = 3{\cdot}3813$, $\sqrt{L_{II}/N} = 1{\cdot}8444$, and $\sqrt{L_{III}/N} = 1{\cdot}8388$. Calculating from the values of the K limit and of K_α, Bohr and Coster give the average level as 3·5, and Sommerfeld as 3·46. The values obtained by Millikan and Bowen are in as good agreement with those calculated from the K series data as could be expected. They are probably correct to about 0·1 per cent.

Again, Sommerfeld[2] shows as stated on p. 260 that the wave-number difference between the L_{II} and L_{III} levels is given by

$$\Delta\nu_L = \Delta\nu_H(Z - s)^4$$

where $\Delta\nu_H$ is the separation of the hydrogen doublet due to the relativity correction[3] and is equal to 0·365 cm.$^{-1}$. As shown above on p. 258, the value of s for the L doublets is 3·5 for the elements of large atomic number. From the observed separation of the magnesium

[1] The values for aluminium and magnesium were given by Bohr and Coster, *Zeitsch. fur Phys.*, **12**, 344 (1923), and that for neon is calculated from the ionisation potential 16·7 volts found by Horton and Davies, *Proc. Roy. Soc.*, A, **98**, 124 (1920). The value for sodium was obtained by interpolation.

[2] *Loc. cit.*, p. 445.

[3] See p. 249.

L doublet, $\nu = 2260$ and with $Z = 12$ the value of s is found to be 3·1, which is not widely different from 3·5. Owing to the interpenetration of the electrons from the M, N, etc., shells in the case of elements of large atomic number Bohr concludes that s should be larger than in the case of elements of small atomic number. In other words, the value of s for elements near neon should be smaller than 3·5, as it is now found to be. Indeed, from the L doublet of neon, as given by Grotrian,[1] and the Sommerfeld relation the value of s for this element is found to be 3·2. This affords a sure proof that the magnesium lines at $\lambda = 323·2$ and 320·9 are, in fact, the L doublet of magnesium.

There remains the sharply defined singlet line at $\lambda = 231·6$ which, if Bohr's general scheme were universally applicable, would be due to the transition from the 3 (2_1) or the M_{II} level to the L_I level. Bohr,[2] however, shows that this level does not exist, this lack being common to all elements giving the alkaline earth type of spectrum. The only M levels, not barred out by the selection principle, which are revealed by the optical series of lines in magnesium are those with wave-number values of $\nu = 39801$ and $\nu = 26620·7$. If one of the electrons of the normal atom of magnesium were in one of these levels, the first with its smaller potential energy would be the more probable, and the transition would be from the M_{III} level to the L_I level. Even if in the normal magnesium atom the two outer electrons are in 3_1 orbits as Bohr places them, yet an electron once displaced from the L_I orbit would have to return to it through a 3_2 orbit and the most probable transition would be that involving the smallest permitted energy change. This would be the transition from the level with $\nu = 39801$ to the L_I level. By the Kossel relation from $\lambda = 231·6$, $\nu = 431800$, the value of the L_I level is found to be 471600, whence $L_I/N = 4·298$ and $\sqrt{L_I/N} = 2·073$.

In Fig. 27 are shown the linear relations between these values of L_I for magnesium, together with those for sodium and neon ($L_I = 184680$, $L_I/N = 1·683$, $\sqrt{L_I/N} = 1·297$, calculated from the highest ionisation potential, 22·8 volts, of neon), and the atomic numbers. The straight line gives an excellent indication that the L_I values are correct.

In the spectrum of aluminium below $\lambda = 1870$ all the strongest lines belong to the spectrum of Al III., where the atom is stripped of all its valency electrons. It was at first believed that a pair of weak lines at $\lambda = 144·3$ and 136·6 were the L doublet, but for theoretical reasons it was afterwards concluded that they are due to oxygen. In the normal aluminium atom the three outer or M electrons are in the 3_1 and 3_2 levels, and consequently when an L electron is displaced it is to be expected that it will be most frequently replaced from the 3_1 or 3_2 level. No 3_1 level has, however, been observed spectroscopically in normal aluminium, so that the transition to be expected

[1] *Zeitsch. für Phys.*, **8**, 116 (1921). [2] *Ann. der Phys.*, **71**, 281 (1923).

is from the observed 3_2 level ($\nu = 48168$) to the L_I or the L_{II}, L_{III} levels, the latter being too close to be resolved in the present work. If this is so, it will at once be possible to calculate the wave-number values of the L levels when the lines due to these transitions are recognised. Taking the two observed lines at $\lambda = 200{\cdot}0$, $\nu = 499950$, and $\lambda = 162{\cdot}4$, $\nu = 615839$, it is found from the Kossel relation that $L_I = 664000$ and $L_{II}L_{III} = 548200$.

Again, Paschen located the 3_1, 3_2, and 3_3 levels in the Al III. spectrum at $\nu = 229450$, 175600, and 113500, and since we know that Al III. lines are present in the extreme ultra-violet spectrum as

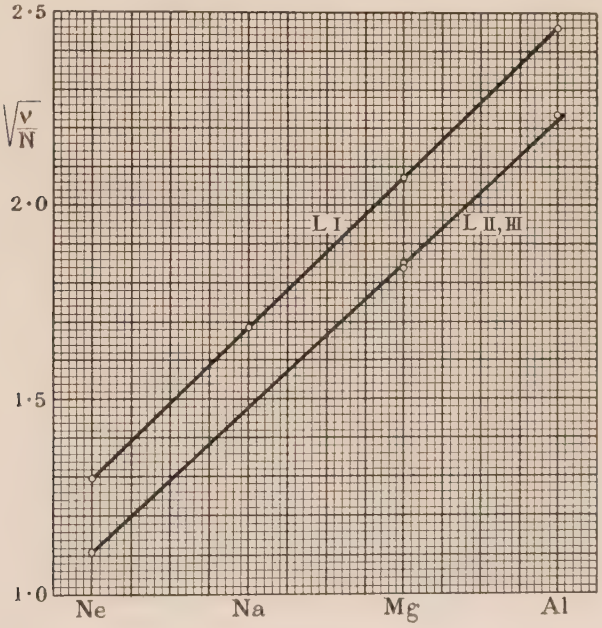


FIG. 27.

observed by Millikan and Bowen, it may be expected that transitions will occur from these levels to the L_I and L_{II} L_{III} levels. In the case of sodium the only transition detected was that from the 3_1 level to the L_I level, and so it may be assumed that this is also the most probable transition in the case of aluminium. In this way the value of L_I in aluminium is found from a line at $\lambda = 230{\cdot}8$, $\nu = 433332$, to be $L_I = 662800$. This value differs from the above value of 664000 by an amount which is well within the observational error.

There is another observed 3_3 level, $\nu = 15845$, in the Al I. spectrum, and the only transition permitted by the selection principle is from this to the L_{III} level. Assuming that this transition takes

place and gives rise to the line at $\lambda = 186{\cdot}9$, $\nu = 534988$, we find that $L_{III} = 550800$. The agreement with the previous value of 548200 is not so good as that for the L_I level, but an error of 0·4 A. in the wave-length measurement would account for the difference. The means of the two values are $L_I = 663400$, $L_{II}L_{III} = 549500$.

An independent check on these values can be obtained in the following way. We have $L_I/N = 6{\cdot}045$, $\sqrt{L_I/N} = 2{\cdot}459$, $L_{II}L_{III}/N = 5{\cdot}008$, $\sqrt{L_{II}L_{III}/N} = 2{\cdot}238$. The straight line in Fig. 27 shows that the L_I value lies in exactly the correct place as indicated by those for neon, sodium, and magnesium. The $L_{II}L_{III}$ value is, on the other hand, a little greater than that given by the straight line, and this raises a question as to the correctness of the value found for aluminium. Millikan and Bowen, however, point out that the four lines at $\lambda = 230{\cdot}8$, 200·0, 186·9, and 162·4, are the only ones out of the seven lines observed in this region which seem to be due to any possible transitions, even though Paschen's values of the Al II. levels have been tried.

The next element which may be considered is calcium, which shows a few strong lines and a considerable number of faint ones between $\lambda = 1303{\cdot}6$ and $\lambda = 312{\cdot}9$. Millikan and Bowen were able to fit some of the former into the Bohr theory in the same way as was used in the case of magnesium. As may be seen from Table CXII., on p. 241, calcium has eight electrons in the M shell and two in N orbits, and we are therefore concerned with the M doublets. The separation of the $M_{II}M_{III}$ doublet is given by Sommerfeld as

$$\Delta\nu = 0{\cdot}108(Z - s)^4.$$

Assuming that the strong pair at $\lambda = 669{\cdot}6$, $\nu = 149350$, and $\lambda = 655{\cdot}9$, $\nu = 152460$ is the $M_{II}M_{III}$ doublet of calcium, then, since $\Delta\nu = 3110$, we find that $s = 7$. The value calculated by Sommerfeld is $s = 8{\cdot}3$, but the M shell of calcium is not complete and consequently a value smaller than 8·3 is to be expected. For that reason the value found is sufficiently close to that calculated to justify the conclusion that the doublet is, in fact, the $M_{II}M_{III}$ doublet of calcium.

It is now possible to calculate the wave-number values of the M_{II} and M_{III} levels from the known value of the N_I level, which is the limit of the principal series of calcium singlets, $\nu = 49305$. The values obtained are

$$M_{II} = 201770,\quad M_{II}/N = 1{\cdot}8387,\quad \sqrt{M_{II}/N} = 1{\cdot}3560.$$
$$M_{III} = 198660,\quad M_{III}/N = 1{\cdot}8104,\quad \sqrt{M_{III}/N} = 1{\cdot}3455.$$

In a later paper Bowen and Millikan [1] discuss the series spectrum of the B. III. atom, which is a stripped atom in the sense that its spectrum is hydrogen-like, being due to one single electron moving between the series of levels characteristic of a simple nucleus-electron system. For such a system the Bohr theory in its elementary form

[1] *Proc. Nat. Acad. Sci.*, **10**, 199 (1924).

for circular orbits led to the result that the constant term in the Rydberg formula increased in the ratio N, 4N, 9N, 16N. As has already been shown in this chapter this simple relation holds good in the cases of Na I., Mg II., and Al III. This is shown by the wave-number values of the 4_4 circular orbits or fundamental orbits which are as follows:—

Theory.	Na I.	Mg II.	Al III.
6858·44	6860·4	6866·8	6871·28

When, however, the orbit is highly elliptical this simple relation does not hold, as is evidenced by the following term values for the 3_1 orbits:—

Theory.	Na I.	Mg II.	Al III.
12192·78	41449·00	30316·9	25494·89

It should be possible in the case of the stripped boron or B III. atom to predict with the greatest accuracy the lines due to the transitions between the circular orbits of the larger radii. Thus the jump from the 5_5 to the 4_4 orbit $(4f - 5g)$ should give a line with wave-number

$$\nu = 9N_B\left(\frac{1}{4^2} - \frac{1}{5^2}\right) = 9 \times 109732\left(\frac{1}{16} - \frac{1}{25}\right) = 2221$$

or $\lambda = 4500{\cdot}3.$

In their work on the extreme ultra-violet spectrum of boron Bowen and Millikan also photographed the visible spectrum and found a new line at $\lambda = 4499{\cdot}0$, which is exactly in the place predicted to within 1 part in 3000.

The next transition to be considered is that between the 4_4 and 3_3 orbits $(3d - 4f)$ and the wave-number should be given by the above formula when the values 5 and 4 are respectively substituted by 4 and 3. This gives $\lambda = 2083$. The divergence from the elementary theory, however, becomes greater the smaller are the orbits, presumably owing to the increased action of the electrons in the K shell. A better method of the calculation of the wave-length of the line is to divide that of the corresponding lithium line, $\lambda = 18697$, by 9. This gives $\lambda = 2077{\cdot}4$. The observed wave-length of the B III. line was 2077·79, which agrees with the calculated value to within 1 in 5000.

The next transition is from the 3_3 orbit to the 2_2 orbit $(2p - 3d)$, but in the alkali type of spectra the 2_2 level is double and we have $2p_1 - 3d$ and $2p_2 - 3d$, so that a narrow doublet is to be expected. The corresponding lithium line is $\lambda = 6103$, and this on division by 9 gives $\lambda = 678$, which is within about one Ångström of the strong B III. line, $\lambda = 676{\cdot}8$, published in the previous paper. It is now found under higher resolving power to be a doublet with $\lambda = 677{\cdot}16$ and 677·01, with $\Delta\nu = 32{\cdot}7$.

There should, of course, also be a doublet with the same separation due to the transition from the 3_1 orbit to the p_1 and p_2 levels, which

would give the first pair of the sharp series. There is only one other doublet below $\lambda = 2000$, namely, that at $\lambda = 758{\cdot}68$, $\nu = 131807{\cdot}9$, and $\lambda = 758{\cdot}47$, $\nu = 131844{\cdot}4$, with a separation of $\Delta\nu = 36{\cdot}5$.

There only remains one other transition, namely, that which gives the first doublet of the principal series, and Bowen and Millikan identify this in the lines $\lambda = 2067{\cdot}88$, $\nu = 48358{\cdot}7$, and $\lambda = 2066{\cdot}41$, $\nu = 48393{\cdot}1$, with $\Delta\nu = 34{\cdot}4$. This exhausts all the B III. lines which can be expected to appear in any strength, and all of them have been found where they should be and with the right separation.

We may now return to the L and M doublets, which were discussed in a preliminary way above.

Now, Millikan and Bowen have proved that the laws of the regular and irregular doublets, established from X-ray observations, are also valid in the optical region.[1] For example, if the regular L doublets of the one-electron-systems, Li I., Be II., B III., C IV., N V., be considered and the relativity formula be used to obtain the values of the screening constant, the values shown in Table CXV. are obtained.

TABLE CXV.

	$2p_2 - 2p_1$.			$3p_2 - 3p_1$.		
	$\Delta\nu$.	$\sqrt[4]{\Delta\nu/0{\cdot}365}$.	s.	$\Delta\nu$.	$\sqrt[4]{\Delta\nu/0{\cdot}108}$.	s.
Li I.	0·338	0·981	2·019	—	—	—
Be II.	6·61	2·063	1·937	—	—	—
B III.	34·4	3·116	1·884	—	—	—
C IV.	107·4	4·142	1·858	31·4	4·128	1·872
N V.	259·1	5·162	1·838	—	—	—

If the two electrons in the K shell acted exactly as if they were in the nucleus itself, the value of s should of course be 2 in each case. The regular progression as Z increases is to be expected from the necessary diminution in the perfectness of the screening of the nucleus by the two K electrons as the ratio of the distance from the nucleus to the outer L electron to the distance from the nucleus to the K electrons decreases. The application of the M doublet formula to the separation 31·4 of the carbon doublet at $\lambda = 5812$ and 5801, which Fowler attributed to C IV., gives almost the same value of s as does the L doublet.

The N V. doublet, the first term of the principal series of the stripped nitrogen atom, was expected to lie at $\lambda = 1240$. On examination of the second order grating spectrum a doublet was found at $\lambda = 2480$, which gave the values of $\Delta\nu$ and s, as shown in Table CXV.

The next systems giving doublets are the three-electron-systems, B I., C II., N III., and O IV. The doublet system of B I. has

[1] Bowen and Millikan, *Phys. Rev.*, **24**, 209 (1924).

already been recognised, and the pair at $\lambda = 2497$ has the separation $\Delta\nu = 15{\cdot}3$. Two new doublets at $\lambda = 2089$ and 1826 measured by Bowen and Millikan [1] have $\Delta\nu = 15{\cdot}8$ and $16{\cdot}2$, respectively. The weighted mean of these three values is $15{\cdot}15$, and on applying the L relativity formula the results shown in the first row of Table CXVI. are obtained. The value $s = 2{\cdot}45$ compared with $s = 1{\cdot}88$ for B III. is to be expected, since the two additional electrons in B I. must exert mutual repulsions and hence decrease the effective nuclear charge. Indeed, the difference gives the first direct measurement of the influence which the additional electrons exert upon the effective nuclear charge.

TABLE CXVI.

	$2p_2 - 2p_1$.			$3p_2 - 3p$.		
	$\Delta\nu$.	$\sqrt[4]{\Delta\nu/0{\cdot}365}$.	s.	$\Delta\nu$.	$\sqrt[4]{\Delta\nu/0{\cdot}108}$.	s.
B I. .	15·55	2·555	2·445	—	—	—
C II. .	66·76	3·678	2·322	10·8	3·161	2·839
N III. .	179·3	4·708	2·292	36·04	4·273	2·727
O IV. .	398·4	5·748	2·252	—	—	—

The C II. separation is that shown by the doublet at $\lambda = 1335$ and, though Fowler does not include this amongst C II. lines, it must belong either to C II. or C IV., and its separation does not agree with its allocation to C IV. The same separation is shown by the carbon doublet at $\lambda = 1036$, and this is also assigned to C II. Moreover, the value of s found, 2·322, is exactly that to be expected from the progression shown in Table CXV.

The extreme ultra-violet spectrum of nitrogen under high resolving power shows only three doublets, namely, one at $\lambda = 991$ with $\Delta\nu = 179{\cdot}3$, and the others at $\lambda = 1744$ and 1493 with $\Delta\nu = 85{\cdot}3$. The first gives the results shown in Table CXVI., whilst the two latter fit the results given in Table CXVII., and consequently must belong to N I. These results show the extreme value of this method of recognising the atomic origin of given spectrum lines.

The oxygen spectrum [2] only shows one strong doublet at $\lambda = 790{\cdot}22$ and 787·74, which also falls in about the right position as given for an O IV. doublet by the progression in s. This gives the value of s shown in the table. A weak oxygen doublet at $\lambda = 658{\cdot}4$ and 656·7 shows the same separation, and, therefore, belongs to O IV. The

[1] *Proc. Nat. Acad. Sci.*, **10**, 199 (1924).
[2] Bowen and Millikan, *Phil. Mag.*, **48**, 259 (1924).

application of the M relativity formula to the doublet separation of 10·8 for C II. and of 36·04 for N III., determined by Fowler, gives the results shown in the right-hand side of Table CXVI. As can be seen the values of s from the M doublets are materially greater than those from the L doublets, whereas in the one-electron-systems the M and L values were nearly identical. Bowen and Millikan point out that this finds a very beautiful interpretation in terms of the shapes of the orbits in the Bohr-Sommerfeld theory. In C II., for example, the M orbit is an ellipse which carries its electron far beyond the L orbits in which the other two valency electrons are found. The result is that in the outer portion of its orbit the M electron is effectively screened by these two L electrons. This increases s to beyond its value when all three electrons are in L orbits and each of them is never more than partially screened by the other two. In the case of C IV., whether the single electron is in the L or M orbit, it is always far outside the region of the K electrons, and hence is almost completely screened in either case.

As regards five-electron-systems, *e.g.* N I. and O II., the N I. doublet has already been mentioned. The relativity formula gives $s = 3{\cdot}090$, as shown in Table CXVII.

TABLE CXVII.

	$2p_2 - 2p_1$.		
	$\Delta\nu$.	$\sqrt[4]{\Delta\nu/0{\cdot}365}$.	s.
N I. .	85·3	3·910	3·090
O II. .	240·0	5·064	2·936

The O II. doublet giving the separation 240·0 is a weak one at $\lambda = 923{\cdot}1$ and $921{\cdot}1$, and is not strong enough for examination under high resolving power. The value of s, therefore, is somewhat uncertain.

The value of s fits well into the progression of this quantity already mentioned. Since in general the value of s is high with small values of the effective nuclear charge and decreases towards a limit as this increases, this limit may be put at 2·8 for five-electron-systems, as compared with 2·2 and 1·8 for the three- and one-electron-systems respectively.

As was stated above, in the case of the eight-electron-system constituting the L shell, $s = 3{\cdot}1$ for the L doublet of magnesium and 3·2 for the same doublet in neon. All the values of s now recorded are consistent with one another and with the fact that in atoms of high atomic number with a whole group of shells completely filled with electrons the value of s found from X-ray observations is 3·5.

The success attending the applicability of the relativity formula to the regular L doublets in the optical region is so marked that it becomes of great interest to see if the irregular doublets in the optical region obey the law found in the case of the Röntgen region. In the optical region the $L_{II}L_{III}$ levels correspond to the $2p_2$, $2p_1$ levels, and the only level for the L_I level to correspond to is the $2s$ level, *i.e.* for the irregular doublet $\Delta\nu = 2s - 2p_2$. In Table CXVIII. are given the values of $\Delta\nu$ for the irregular L doublets for one-electron-systems, and in the last column the values of $\sqrt{\nu_s} - \sqrt{\nu_p}$, which, according to the Hertz law, should be approximately constant. There can be no doubt from these results that the laws of both regular and irregular doublets, first discovered in the field of X-rays, are equally applicable to the optical region.

TABLE CXVIII.

	$2s - 2p_2$.		
	$\Delta\nu$.	Diff.	$\sqrt{\nu_s} - \sqrt{\nu_p}$.
Li I. .	14903·8		39·470
		17023·8	
Be II. .	31927·6		44·297
		16431·1	
B III. .	48358·7		45·594
		16122·5	
C IV. .	64481·2		46·068
		15973·9	
N V. .	80455·1		46·276

In Table CXIX. are given the doublet separations and the values of the screening constant calculated from the relevant relativity formula. The separations of the $3p$ terms for Na I., Mg II., Al III., and Si IV. are known from the work of Fowler, Paschen, and others, whilst that for P V. was determined by Millikan and Bowen. From the systematic progression in the values of s it is possible to calculate its value for S VI. Further, the wave-numbers of this S VI. doublet can be calculated from the irregular doublet separation which, as was seen in Table CXVIII., is the observed wave-number. Since the linear progression at this point indicates the addition of about 17200, the wave-number of the $3s - 3p_2$ line for S VI. should be about $88670 + 17200 = 105870$, where, as may be seen from Table CXX., 88670 is the irregular doublet separation for P V. Millikan and Bowen in their first investigation found a line at $\lambda = 945{\cdot}0$, $\nu = 105826$, which is extremely close to the calculated value, and another line at $\lambda = 933{\cdot}7$, $\nu = 107105$, the difference $\Delta\nu = 1279$ being again very near the calculated value. These numbers show that this doublet with great certainty can be assigned to S VI. and also that this method

of predicting the separation and location of a doublet arising from a given type of ionisation is free from ambiguity.

TABLE CXIX.

	$3p_2 - 3p_1$.			$4p_2 - 4p_1$.		
	$\Delta\nu$.	$\sqrt[4]{\Delta\nu/0{\cdot}108}$.	s.	$\Delta\nu$.	$\sqrt[4]{\Delta\nu/0{\cdot}0456}$.	s.
Na I. .	17·18	3·550	7·450	5·49	3·312	7·688
Mg II. .	91·55	5·394	6·606	30·5	5·085	6·915
Al III. .	238	6·849	6·151	80·13	6·474	6·526
Si IV. .	460	8·076	5·924	162·06	7·720	6·280
P V. .	795	9·260	5·740	—	—	—
S VI. .	1279	10·428	5·572	—	—	—

	$5p_2 - 5p_1$.			$6p_2 - 6p_1$.		
	$\Delta\nu$.	$\sqrt[4]{\Delta\nu/0{\cdot}0234}$.	s.	$\Delta\nu$.	$\sqrt[4]{\Delta\nu/0{\cdot}0135}$.	s.
Na I. .	2·49	3·213	7·787	1·50	3·246	7·754
Mg II. .	14·07	4·954	7·046	7·6	4·869	7·131
Al III. .	39·15	6·398	6·602	—	—	—
Si IV. .	75	7·528	6·472	41	7·421	6·579

	$3d_2 - 3d_1$.			$4d_2 - 4d_1$.		
	$\Delta\nu$.	$\sqrt[4]{\Delta\nu/0{\cdot}036}$.	s.	$\Delta\nu$.	$\sqrt[4]{\Delta\nu/0{\cdot}0152}$.	s.
Mg II. .	0·99	2·289	9·711	—	—	—
Al III. .	2·28	2·820	10·180	1·28	3·029	9·971

	$4f_2 - 4f_1$.		
	$\Delta\nu$.	$\sqrt[4]{\Delta\nu/0{\cdot}0076}$.	s.
Al III. .	0·38	2·659	10·341
Si IV. .	1·26	3·588	10·412

The values of s for the $4p$ terms are calculated from the relativity formula for the $N_{II}N_{III}$ levels, and the closeness of these to those for the $3p$ terms affords further evidence of the general correctness of

the relativity formula. Still further evidence is gained from the values for the $5p$ and $6p$ levels.

The data for the two irregular M doublets are given in Table CXX.

TABLE CXX.

	$3s - 2p_2$.			$3p_1 - 3d_2$.		
	$\Delta\nu$.	Diff.	$\sqrt{\nu_s} - \sqrt{\nu_p}$.	$\Delta\nu$.	Diff.	$\sqrt{\nu_s} - \sqrt{\nu_p}$.
Na I. .	16956·2		47·089	12199·5		45·649
		18713·2			23529·9	
Mg II. .	35669·4		55·666	35729·4		69·307
		18010·4			26307·8	
Al III. .	53679·8		59·759	62037·2		82·074
		17600·2			26585·8	
Si IV. .	71280		62·277	88623		89·382
		17390			25345	
P V. .	88670		64·115	113968		93·077
		17156				
S VI. .	105826		65·522			

Since, in Table CXIX. we are dealing with a single electron in an orbit of higher quantum number than those of the K and L shells, and since these are completely filled with two and eight electrons respectively, it follows that the screening constant s must be 10 when the single electron is in an orbit which is completely outside the L shell. This last condition is satisfied by the $3d$, $4d$, and $4f$ terms, since these are hydrogen-like, and as can be seen, the value of s for these terms is equal to 10 within the limits of measurement of $\Delta\nu$.

Again, the fact that the values of s for the $3p$ terms are less than 10 may be taken as being due to the interpenetration by the $3p$ electrons into the inner portion of the atom where the screening from the nucleus by the ten K and L electrons is very imperfect. Also the progression in s from 7·45 to 5·57 is to be explained by the decrease in the screening as the single electron becomes closer and closer to the nucleus in comparison with the distance from the nucleus of the L shell of electrons.

The remarkable success of the relativity formula is most strikingly shown when it is applied to triplets. Thus the separation of the wider components of the $2p$ triplet of Be I. is given by Paschen as 2·34 A. From this it is found that $s = 2{\cdot}409$. The value of s for Be II. was given above as 1·937, and, since Be II. has only one electron in the L shell and Be I. has two, it will be recognised that not only does the relativity fourth power law hold, but also that the value 2·41 is about right. Again, the application of the M doublet relativity formula to the separation $\Delta\nu = 13$ of the $3p$ triplet of C III. (Fowler) gives $s = 2{\cdot}69$, which is consistent with $s = 2{\cdot}830$ for C II.

given above, seeing that the latter has one more electron than the former.

In Table CXXI. are given the data of the L triplets of C I., N II., and O III., and here, since we now have a four-electron system, the values of s should be greater than in the case of the three-electron systems, as, indeed, they are found to be.

TABLE CXXI.

	$2p_2 - 2p_1$.		
	$\Delta\nu$.	$\sqrt[4]{\Delta\nu/0{\cdot}365}$.	s.
C I. .	27·8	2·95	3·05
N II. .	82·1	3·873	3·127
O III. .	199·7	4·836	3·164

In Table CXXII. are given the values of s calculated by the M and N relativity formulæ from the wider pair of the triplets of Mg I., Al II., Si III., and P IV.

TABLE CXXII.

	$3p_2 - 3p_1$.			$4p_2 - 4p_1$.		
	$\Delta\nu$.	$\sqrt[4]{\Delta\nu/0{\cdot}108}$.	s.	$\Delta\nu$.	$\sqrt[4]{\Delta\nu/0{\cdot}0456}$.	s.
Mg I. .	40·9	4·410	7·590	4·1	3·079	8·921
Al II. .	125·5	5·837	7·163	29·18	5·029	7·971
Si III. .	257	6·982	7·018	—	—	—
P IV. .	439	7·982	7·018	—	—	—

The results of the foregoing point very definitely to the fact that, provided the orbits from which the values of $\Delta\nu$ are obtained lie far outside the screening electrons, the values of s of 2 for L orbits, 10 for M orbits, etc., are given by the fourth-power relativity formula. Under the same proviso the same results are given by the simple Moseley-Bohr formula—[1]

$$\nu = \frac{N}{n^2}(Z - s)^2$$

as shown by Table CXXIII.

[1] Millikan and Bowen, *Phys. Rev.*, **24**, 223 (1924).

TABLE CXXIII.

	$2p_1$.		$3d_1$.		$4f_1$.	
	ν.	s.	ν.	s.	ν.	s.
Li I. .	28582·5	1·979287	12203·1	1·999586	6856·1	2·000180
B III.	257545	1·936062	109870	1·998183	61742	1·999637
Na I. .	24475·65	9·583189	12276·18	9·996595	6860·37	9·999868
Mg II.	85506·44	9·351841	49776·0	9·979519	27467·4	9·998792
Al III.	175536·11	9·205732	113496·68	9·949042	61841·56	9·997219
Si IV.	292377	9·103155	203705	9·912615	109923	9·996612

The remarkable success of the two formulæ in giving in the optical field the known values of s is very significant and establishes the validity of the theoretical conceptions which underlie both. It may be pointed out that when the radiating orbits approach too close to the screening electrons it is not to be expected that the same average value of s will be obtained from the former involving $(Z - s)^4$ as in the latter which contains the term $(Z - s)^2$.

Millikan and Bowen point out that the foregoing results lead to very elegant simplifications in the rules which define spectroscopic behaviour. They require, in the first place, an extension of a well-established optical rule into the X-ray field in definitely identifying the L_I, M_I, N_I, X-ray levels with the s-terms of optical series, also L_{II} L_{III}, M_{II} M_{III}, etc., levels with p_2 p_1 terms, and the M_{IV} M_V, etc., levels with d_2 d_1 terms, and so on. This was suggested by de Broglie and Dauvillier,[1] and by Landé.[2]

In the second place, the results extend the laws of the regular and irregular doublets from the X-ray field so as to cover the whole field of optics. The irregular doublet law states that the frequency difference between the L_I and L_{II} terms increases linearly with the atomic number for similar structures; it has already been shown above that this is the case for the difference between the s and p_2 terms. The relativity doublet law states that the fourth root of the separations of the L_{II} and L_{III} terms progresses linearly with the atomic number for similar structures. This progression in the separations in the p, d, and f terms has been shown in the foregoing tables.

In the third place, they show that the same selection principles must apply to the azimuthal and inner quantum numbers in the two fields.

Millikan and Bowen, however, point out that a very serious difficulty arises in connection with this identification of the L_{II} L_{III} orbits with the p_2 p_1 orbits. It is generally agreed that the L_{II} L_{III} orbits are 2_1 2_2 orbits, respectively, and this must be the case if they

[1] *Comptes Rend.*, **175**, 722 (1922).
[2] *Zeitsch. für Phys.*, **16**, 391 (1923).

really constitute a relativity doublet. On the other hand, if it be accepted that the p_2 p_1 orbits are 2_1 2_2 orbits and not both 2_2 orbits with their difference in frequency due to a change in their inner quantum numbers, the validity of the Bohr conception of the interpenetration of orbits is entirely overthrown. In addition to this we find the following three specific difficulties :—

1. The p_2 p_1 orbits, in spite of their widely different shapes, actually possess the same screening constant, their frequencies being so near together that no appreciable difference in the value of the screening constant can be found.

2. If the p_2 p_1 orbits are 2_1 2_2 orbits, the s or L_1 orbit must also have the form 2_1, the difference between it and p_2 being due to an inner quantum number. That being so the values for the screening constant for the s and p terms should be very nearly the same, but in fact, since the s term has a much greater frequency than p_1, the value of the screening constant as determined by the Moseley-Bohr equation is much smaller than that of p_1.

To avoid these two difficulties it is necessary to make the very unnatural assumption that the inner quantum number, *i.e.* the orientation of the orbit with respect to the atom body, has a much more powerful effect upon the screening constant s than has the wide difference of the shape of the orbit represented by the difference between 2_1 and 2_2. In a word, the behaviour of the s, p, d, f, etc., terms speaks for the retention of the assignment of the azimuthal quantum numbers 1, 2, 3, 4, etc., to these terms, respectively.

3. In the spectra of Be I., B II., C III., etc., as in the case of all the alkaline earth metals there are three p orbits designated as p_1, p_2, p_3, whilst, since such orbits have a total quantum number of 2, the relativity theory permits but two different shapes, *i.e.* but one relativity doublet. In this case the additional p level must in any case be assigned to a change in an inner quantum number instead of to a change in an azimuthal quantum number. If such a change in orientation is responsible for the difference between p_2 and p_3, it is at least natural to assume that the difference in energy between p_2 and p_1 is also due to such a change in orientation. In other words, the existence of these three levels is a strong argument in favour of explaining all of these fine-structure differences by differences in orientation and leaving the differences in the shapes of orbits to explain the large differences between the s and p terms. This is one of the strongest arguments for the usual assignment of azimuthal and inner quantum numbers in the optical region.

The only way in which it appears to be possible to avoid the foregoing serious difficulties is to throw overboard altogether the relativity explanation of the regular doublet and to assume that the amazing success of the relativity formula in predicting the correct numerical values of the screening constant is not due to differences in the shapes of elliptical and circular orbits, as postulated by the relativity theory of doublet separations, but that there is some other

cause which by mere chance leads exactly to this relativity formula without actually necessitating relativity conceptions.

In view of the fact, however, that this relativity formula was deduced from purely theoretical considerations involving no arbitrary constants whatever and that it nevertheless predicts quantitatively not only the whole fine line structure of the spectra of H and He^+, which are definitely known to be simple nucleus-electron systems, but also the correct screening constants 2 and 10 as shown above, it is almost unbelievable that the fundamental conception underlying the development of the formula has no basis whatever in reality.

Again, if we discard the relativity explanation of the p_2 p_1 terms and of the L_{II} L_{III} terms, making these two orbits of like shape and letting them differ only in inner quantum number and consequently assigning different shapes (different azimuthal numbers) to the s and p_2 terms, there must still be a relativity effect separating the values of the s and p terms, since the first is elliptical and the second circular. When, now, atomic numbers are high, this necessitates a relativity separation between the s and p_2 (L_I and L_{II}) terms which is much larger than the observed separation. Indeed, for higher atomic numbers $L_{II}L_{III}$ are actually separated four or five times as much as are L_IL_{II}, so that it becomes altogether impossible to assign L_I L_{II} to different azimuthal quantum numbers, unless we deny that the electrons in these orbits are subject to the laws of relativity at all.

These results force a choice between one or the other of the two horns of a dilemma, which may be stated thus: (1) the abandonment of relativity causes and effects altogether in electronic orbits, or (2) the abandonment of Bohr's interpenetration ideas, and with them the practice of assigning azimuthal quantum numbers 1, 2, 3, 4, etc., to s, p, d, f, etc., terms, respectively. In this case some way must be found to permit two orbits which have the same shape (azimuthal quantum numbers) but different orientations (inner quantum numbers) to possess widely different screening constants. This would seem to require the introduction of a dissymmetry not heretofore contemplated in atomic models. The only escape from one or other of these conclusions is to discredit the foregoing evidence for the correspondence between the s and the L_I levels and between the p_2 p_1 and the L_{II} L_{III} levels.

This cardinal difficulty is discussed in a later paper by Millikan and Bowen,[1] who put forward a possible method of reconciliating the Bohr interpenetration conception with the Sommerfeld relativistic treatment of electron orbits. They suggest that the only escape from the dilemma is to find some break in the continuity of the proof of the exact applicability of the relativity formula to all atoms from uranium to hydrogen. It is just possible to make such a break between ionised helium and lithium, and thus save the relativity explanation for simple systems like H and He^+, where the evidence for its validity

[1] *Phil. Mag.*, **49**, 923 (1925); *Proc. Nat. Acad. Sci.*, **11**, 119 (1925).

is wonderfully exact. In order to do this it is necessary to make a very difficult and strange assumption, namely, that the remarkable applicability of the relativity formula to all atoms from lithium to chlorine and to all the X-ray phenomena is accidental, and that there must be present some other cause, non-relativistic, which is responsible for the spectral characteristics of these elements. This cause, though it is concerned with inner quantum numbers rather than azimuthal, must lead not only to the fourth power law, but also to a formula with the same numerical constants as those of the relativity law.

The two remarkable successes of the relativity formula found by Millikan and Bowen may be re-stated.

(1) The fairly close prediction which it makes of the screening due to the two K electrons in the spectra of the stripped atoms from lithium through nitrogen.

(2) The extraordinarily accurate prediction of the variation of doublet separation with change in total quantum number.

By making their choice that the $2p_1$ $2p_2$ orbits are circles differing only in orientation (inner quantum number) Millikan and Bowen make the definite assumptions that the above relativity formula successes are purely accidental and that the separation of the $2p_1$ $2p_2$ terms is due to some other cause which leads not only to the same type of variation in $\Delta\nu$ with atomic number and total quantum number as does the relativity formula, but also to very nearly the same numerical constants.

In view of this it becomes essential to re-examine all the data in order to see how precisely the relativity formula does actually fit these data. Before making this analysis Millikan and Bowen state their assumptions and their conclusions as to the requirements which must be imposed on the new cause. The assumptions are as follows :—

(*a*) That in a simple nucleus-electron system the fine structure of lines is entirely due to relativity, so that the character of the H and He^+ lines is fully explained by the Sommerfeld relativity equation —[1]

$$\frac{\nu}{N} = \frac{(Z-\sigma)^2}{n^2} + \frac{\alpha^2}{n^4}(Z-s)^4\left(\frac{n}{k} - \frac{3}{4}\right) + \ldots$$

(*b*) That the selection principle used in optical spectra is applicable to all radiation, and that L_I like $2s$ is a 2_1 orbit, also that L_{II} L_{III} like p_2 and p_1 are circular orbits which differ only in orientation.

(*c*) That the L_I and L_{III} orbits, like the $2s$ and $2p_1$ orbits, are an ellipse (2_1) and a circle (2_2), respectively, the energies of which differ, first, because of the difference in the greater screening of the circular orbit, and, second, because of the relativity difference between the two orbits. This is equivalent to assuming that the $L_I L_{III}$ orbits differ in energy by the sum of the irregular doublet energy difference and the regular doublet energy difference. In the field of optics the

[1] See p. 261.

first difference is very large compared with the second, whilst in the field of X-rays the opposite is the case.

With the aid of these three assumptions Millikan and Bowen retain the application of relativity to all orbits. Their principal assumption is :—

(*d*) That there is some cause acting by virtue of the difference in orientation of the two circular orbits I_{II} and I_{III} which increases the energy of the former to about the same amount which it would have had by virtue of relativity had it been a 2_1 orbit.

The advantage of this assumption over that of entirely discarding the applicability of relativity to electron orbits is that it is not now necessary that the new cause give results which are in such exact coincidence with those given by the Sommerfeld equation as would be demanded if the new cause were required to fit the extraordinarily accurate data on H and He^+.

In analysing the doublet separation data of the atoms from lithium to uranium, Millikan and Bowen find that they may be distinguished from the data available with a simple nucleus-electron system.

1. They differ qualitatively in the fact that all those elements have at least three two-quantum-number levels, namely, the $2s$, $2p_2$, $2p_1$ or L_I, L_{II}, L_{III} levels, whilst in H and He^+ there are only the two levels required by the relativity theory.

2. They differ quantitatively in the fact that whilst the Sommerfeld equation fits the data from H and He^+ where $s = \sigma = 0$, this cannot be asserted for any other systems. Indeed, by subtracting two equations of the Sommerfeld type, corresponding to the two azimuthal quantum numbers 2 and 1, which gives

$$\Delta\nu = \frac{N\alpha^2(Z - s)^4}{n^3k(k - 1)},$$

where $k = 2$, the practice has been to solve for s, which then becomes an arbitrary parameter. For the whole series of stripped atoms, commencing with lithium, the value of s should be 2, since there are in each case two screening electrons. We have already seen that the values of s are

	s.
Li	2·019
Be II. . . .	1·937
B III. . . .	1·884
C IV. . . .	1·858
N V. . . .	1·838

Not one of these values is really within the limit of experimental error of 2, and, moreover, the fourth power means that a large error in $\Delta\nu$ means a small error in s.

It is true that Millikan and Bowen did suggest a logical explanation for the last four of these departures for the true value of 2, but they now show that the value of 2·019 is greater than 2 by an amount which is six times that allowable by experimental error. It is of

course impossible for the screening constant for an L orbit to be greater than 2, however far the radiating electron is removed. As they say, the quantity s as used by them is, within rather narrow limits, an arbitrary parameter with the aid of which they forced the relativity formula into agreement with observation.

There is no need to quote the whole of Millikan and Bowen's arguments in favour of their assumption and we quote their concluding sentence. To find a new cause for the relativity doublet formula with only a little leeway in the value of the numerical constants is a problem worthy of the efforts of the theoretical physicist.

In a later paper [1] Bowen and Millikan deal with the series spectra of the stripped atoms, making use of their method for predicting the precise frequencies which must be emitted by an atom in a given state of ionisation, and the precise doublet separations to be expected. They give the series data of the complete series from Na I. to Cl VII., the values of the first five atoms being more accurate than those previously recorded. In Table CXXIV. are detailed the data of the regular doublets as given by the $3p_2 - 3p_1$ separations.

TABLE CXXIV.

	$\Delta\nu$.	s.
Na I.	17·18	7·450
Mg II.	91·55	6·606
Al III.	234·00	6·180
Si IV.	461·84	5·916
P V.	794·82	5·741
S VI.	1267·10	5·596
Cl VII.	1889·5	5·504

The application of the irregular doublet law is shown in Table CXXV.

TABLE CXXV.

	$3s - 3p_1$.	Diff.	Second diff.	$3p_1 - 3d$.	Diff.
Na I.	16956·17			12199·48	
		18713·25			23529·96
Mg II.	35669·42		701·14	35729·44	
		18012·11			26308·34
Al III.	53681·53		408·15	62037·78	
		17603·96			26585·63
Si IV.	71285·49		240·03	88623·41	
		17363·93			26131·82
P V.	88649·42		147·31	114755·23	
		17216·62			25557·64
S VI.	105866·04		81·43	140312·87	
		17135·19			
Cl VII.	123001·23				

[1] *Phys. Rev.*, **25**, 295 (1925).

The validity of the method can be exemplified by one instance. The second differences given in Table CXXV. progress systematically by a factor 0·58, so that it was possible to predict where the first member of the principal series of Cl VII. should be within considerably less than 15 wave-number units (0·1 A.). By the use of aluminium electrodes, cored with NaCl, a line was found at exactly the right place, $\lambda = 813{\cdot}00$. Again, from the progression in the values of s in Table CXXIV. it was evident that for Cl VII. s must be very nearly 5·5. Substitution of this value in the equation $\Delta\nu = 0{\cdot}108(Z - s)^4$ gave a value of $\Delta\nu$ which could not be in error by more than 0·1 A. At precisely the calculated distance from the line $\lambda = 813{\cdot}00$ another line of the same intensity was found at $\lambda = 800{\cdot}70$.

The series lines and terms of P V. and S VI. are given in Tables CXXVI. and CXXVII.

TABLE CXXVI.

SPECTRUM OF STRIPPED PHOSPHORUS, P V.

Int.	λ I.A. (vac.).	ν.	Δ.		Term values.	
2	542·52	184325·0	815·2	$3p_2 - 4s$	$3s$	524491·19
					$4s$	251540·66
2	544·93	183509·8		$3p_1 - 4s$	$5s$	147858·7
3	673·92	148385·6		$3d - 4s$	$3p_1$	435046·95
					$3p_2$	435841·77
4	865·475	115543·49	788·26	$3p_2 - 3d$	$4p_1$	220055·11
					$4p_2$	220339·02
5	871·420	114755·23		$3p_1 - 3d$		
2	997·637	100236·86	277·84	$3d - 4p_1$	$3d$	320295·0
					$4d$	179101·1
2	1000·410	99959·02		$3d - 4p_2$		
					$4f$	171909·4
15	1118·015	89444·24	794·82	$3s - 3p_1$	$5f$	110036·5
12	1128·039	88649·42		$3s - 3p_2$	$5f'$	109818·4
					$6f'$	76278·5
0	1385·11	72196·4		$4p_1 - 5s$		
					$6f''$	76255·2
1	1447·92	69064·6		$4d - 5f$		
2	1610·54	62091·0		$4d - 5f'$		
2	2425·08	41235·75	279·50	$4p_2 - 4d$		
2	2441·63	40956·25		$4p_1 - 4d$		
2	2962·26	33758·0		$5f - 6f'$		
3	2979·45	33563·2		$5f' - 6f''$		
5	3176·06	31485·55	283·91	$4s - 4p_1$		
3	3204·96	31201·64		$4s - 4p_2$		

TABLE CXXVII.

SPECTRUM OF STRIPPED SULPHUR, S VI.

Int.	λ I.A. (vac.).	ν.	Δν.		Term values.	
0	388·91	257128·9	1256·6	$3p_2 - 4s$	$3s$	710264·2
0	390·82	255872·3		$3p_1 - 4s$	$4s$	347264·0
					$3p_1$	603131·1
1	464·63	215225·0		$3d - 4f$	$3p_2$	604398·2
					$4p_1$	308625·9
1	706·503	141542·2	1229·3	$3p_2 - 3d_2$	$4p_2$	309083·5
2	712·693	140312·9		$3p_1 - 3d_1$	$3d_1$	462818·2
0	712·868	140278·4	34·5	$3p_1 - 3d_2$	$3d_2$	462854·4
					$4f$	247612·1
5	933·418	107133·1	1267·1	$3s - 3p_1$	$5f'$	158159·5
4	944·590	105866·0		$3s - 3p_2$		
0	1117·91	89452·6		$4f - 5f'$		
1	2588·12	38638·1	457·6	$4s - 4p_1$		
0	2619·14	38180·5		$4s - 4p_2$		

In a further paper[1] the series spectra of two-electron systems are detailed, and these were obtained by the application of the two doublet laws to the atoms from Mg I. to Cl VI. It will be remembered that whereas the irregular doublet law is here applicable in exactly the same way as in one-electron systems, the two-electron systems are characterised by triplets or singlets and not by doublets. It has already been shown that the relativity doublet law applies to the two lines of the triplet with the greater separation, and in this paper Bowen and Millikan consider the two outside lines of the triplet. They commence by proving that whenever a line follows the irregular doublet law it must be produced by a transition between orbits of the same total quantum number. The simple Moseley law

$$\frac{\nu}{N} = \frac{(Z - \sigma)^2}{n^2}$$

shows that in any transition between two orbits with different screening constants σ_1 and σ_2 and total quantum numbers n_1 and n_2 the wave-number ν' is given by

$$\frac{\nu'}{N} = \frac{(Z - \sigma_1)^2}{{n_1}^2} - \frac{(Z - \sigma_2)^2}{{n_2}^2}$$
$$= \frac{({n_2}^2 - {n_1}^2)Z^2 - 2({n_2}^2\sigma_1 - {n_1}^2\sigma_2)Z + {n_2}^2{\sigma_1}^2 - {n_1}^2{\sigma_2}^2}{{n_1}^2{n_2}^2}.$$

[1] *Phys. Rev.*, **25**, 591 (1925).

It is evident from this that the only condition under which ν' can vary linearly with Z is that $n_2 = n_1$, since the coefficient of Z^2 must be zero. In other words, the irregular doublet law signifies that there is a difference in the value of the screening constant between orbits of the same total quantum number. Since the irregular doublet law also is equivalent to parallelism between the lines given on the Moseley diagram by the two sets of levels which give the doublet, it follows that whenever such parallelism is found the relevant levels in every case have the same total quantum number.

TABLE CXXVIII.

IRREGULAR DOUBLETS.

	$3p_1 - 3d$.		$4s - 4p_3$.	
	ν.	Diff.	ν.	Diff.
Mg I.	26045·9	31926·8	6650·4	7502·73
Al II.	57972·7	31813·3	14153·13	7700·37
Si III.	89786·0	30993·9	21853·5	7802·0
P IV.	120779·9	30017·8	29655·5	7850·9
S V.	150797·7		37506·4	

	$3S - 3P$.		$4p_1 - 4d$.	
	ν.	Diff.	ν.	Diff.
Mg I.	35051·4	24793·7	6340·2	9672·42
Al II.	59845·1	23033·8	16012·62	10250·18
Si III.	82878·9	23311·5	26262·8	10224·1
P IV.	105190·4	21953·6	36486·9	
S V.	127144·0	21805·2		
Cl VI.	148949·2			

TABLE CXXIX.

REGULAR DOUBLETS.

$3p_3 - 3p_1$.

	$\Delta\nu$.	$Z - s$.	s.
Mg I.	60·81	4·870	7·130
Al II.	187·3	6·451	6·549
Si III.	394·0	7·769	6·231
P IV.	696·3	8·958	6·042
S V.	1128·1	10·106	5·894
Cl VI.	1720·1	11·230	5·770

TABLE CXXX.

SERIES LINES OF P IV.

Int.	λ I.A. (vac.).	ν.	$\Delta\nu_p$.	$\Delta\nu_d$.		Term values.	
2	631·74	158293·0			$3p_1 - 4s$	$4s$	187687·9
5	823·21	121476·4	228·6		$3p_3 - 3d$	$5s$	105479·2
6	824·76	121247·8			$3p_2 - 3d$	$3p_1$	345964·9
6	827·95	120779·9	467·9		$3p_1 - 3d$	$3p_2$	346432·8
						$3p_3$	346661·4
4	1025·58	97506·0				$4p_1$	157825·3
4	1028·13	97264·2				$4p_2$	157973·7
4	1030·53	97037·1			pp^* group	$4p_3$	158032·4
4	1033·14	96792·4					
4	1035·54	96567·9				$3d$	225185·0
3	1484·55	67360·5	149·6		$3d - 4p_1$	$4d_1$	121330·7
3	1487·85	67210·9			$3d - 4p_2$	$4d_2$	121338·4
2	1489·16	67152·1	58·8		$3d - 4p_3$	$4d_3$	121344·0
0	1904·97	52494·3	147·9		$4p_2 - 5s$		
0	1910·35	52346·4			$4p_1 - 5s$		
4	2725·67	36688·2			$4p_3 - 4d_3$		
4	2729·61	36635·3	58·2	5·3	$4p_2 - 4d_2$		
3	2730·00	36630·0			$4p_2 - 4d_3$		
5	2740·13	36494·6	148·4	7·7	$4p_1 - 4d_1$		
3	2740·71	36486·9		5·3	$4p_1 - 4d_2$		
		36481·6[1]					
6	3348·67	29862·6	148·4		$4s - 4p_1$		
6	3365·39	29714·2	58·7		$4s - 4p_2$		
5	3372·06	29655·5			$4s - 4p_3$		
10	950·66	105190·4			3S – 3P		

By the use of the irregular and regular doublet laws the lines and term values were found for the series Mg I. to Cl VI. but the details of the procedure need not be given here. The irregular data are given in Table CXXVIII.

The regular doublet data are given in Table CXXIX.

The series lines and terms of P IV., S V., and Cl VI. are given in Tables CXXX., CXXXI., and CXXXII.

[1] Not observed.

TABLE CXXXI.

SERIES LINES OF S V.

Int.	λ I.A. (vac.).	ν.	Δν.		Term values.	
1	437·37	228639·4	427·9	$3p_3 - 4s$	$4s$	273075·0
1	438·19	228211·5	757·8	$3p_2 - 4s$	$3p_1$	500497·7
					$3p_2$	501252·4
1	439·65	227453·7		$3p_1 - 4s$	$3p_3$	501618·2
3	658·25	151918·2	365·8	$3p_3 - 3d$	$4p_1$	235191·6
					$4p_2$	235480·7
4	659·84	151552·4	754·7	$3p_2 - 3d$	$4p_3$	235568·6
4	663·14	150797·7		$3p_1 - 3d$	$3d$	349700·0
4	849·25	117751·1				
4	852·19	117345·0				
5	854·81	116985·6		pp^* group		
4	857·83	116573·2				
4	860·46	116216·9				
1	873·20	114521·3	321·7	$3d - 4p_1$		
1	875·66	114199·6		$3d - 4p_2$		
4	2639·68	37883·4	289·1	$4s - 4p_1$		
2	2659·98	37594·3	87·9	$4s - 4p_2$		
1	2666·21	37506·4		$4s - 4p_3$		
6	786·51	127144·0		3S – 3P		

TABLE CXXXII.

SERIES LINES OF Cl VI.

Int.	λ I.A. (vac.).	ν.	
3	724·13	138096·8	
3	727·54	137449·5	
4	730·31	136928·2	pp^* group.
3	733·89	136260·2	
3	736·76	135729·4	
4	671·37	148949·2	3S – 3P

In their next paper Millikan and Bowen [1] give the series data of three-valency-electron systems, namely, Al I. to Cl V. These are shown in Tables CXXXIII. to CXXXVII.

[1] *Phys. Rev.*, **25**, 600 (1925).

TABLE CXXXIII.

Irregular Doublets.

	$3p_1 - 3d$.		$4s - 4p_2$.	
	ν.	Diff.	ν.	Diff.
Al I.	32324·69	46731·31	7601·57	8090·03
Si II.	79056·0	37265·1	15691·6	7849·6
P III.	116321·1	34868·1	23541·2	8524·0
S IV.	151189·2	33200·4	32065·2	
Cl V.	184389·6			

	$4p_1 - 4d$.	
	ν.	Diff.
Al I.	5967·76	13804·84
Si II.	19772·6	11143·7
P III.	30916·3	10757·5
S IV.	41673·8	

TABLE CXXXIV.

Series Lines of P III.

Int.	λ I.A. (vac.).	ν.	$\Delta\nu$.		Term value.	
2	848·65	117834·2	559·4	$3p_2 - 4s$	$4s$	125497·8
3	852·70	117274·8		$3p_1 - 4s$	$5s$	67292·8
4	855·65	116870·6	549·5	$3p_2 - 3d$	$3p_1$	242772·5
6	859·69	116321·1		$3p_1 - 3d$	$3p_2$	243332·1
4	913·99	109410·7			$4p_1$	101821·2
5	917·14	109035·2	559·8		$4p_2$	101957·8
5	918·69	108850·9	559·2	pp^* group	$3d_1$	126450·0
5	921·86	108476·0			$3d_2$	126461·4
5	998·03	100197·1	559·7	$3p_2 - x$	$4d$	70904·5
5	1003·64	99637·4		$3p_1 - x$	x	143135·1
1	2420·47	41314·3	136·4	$x - 4p_1$		
1	2428·49	41177·9		$x - 4p_2$		
5	2884·75	34665·0	136·6	$4p_2 - 5s$		
5	2896·17	34528·4		$4p_1 - 5s$		

TABLE CXXXIV.—*Continued.*

Int.	λ I.A. (vac.).	ν.	Δν.		Term values.
6	3220·23	31053·7	137·4	$4p_2 - 4d$	
6	3234·54	30916·3		$4p_1 - 4d$	
4	4058·53	24639·5	136·8	$3d_2 - 4p_1$	
6	4060·41	24628·1		$3d_1 - 4p_1$	
7	4081·18	24502·7		$3d_2 - 4p_2$	
7	4223·34	23677·9	136·7	$4s - 4p_1$	
7	4247·87	23541·2		$4s - 4p_2$	

TABLE CXXXV.

SERIES LINES OF S IV.

Int.	λ I.A. (vac.).	ν.	Δν.		Term values.	
2	551·17	181432·2		$3p_2 - 4s$	$4s$	200109·2
5	657·34	152127·8	938·6	$3p_2 - 3d$	$5s$	110531·0
6	661·42	151189·2		$3p_1 - 3d$	$3p_1$	380591·2
					$3p_2$	381541·4
5	744·92	134242·8				
5	748·40	133618·6	950·5	pp^* group	$4p_1$	167824·0
5	750·23	133292·3	950·0		$4p_2$	168034·0
5	753·56	132668·6				
					$3d_1$	229400·0
4	809·69	123503·9	950·1	$3p_2 - x$	$3d_2$	229414·3
5	815·97	122553·8		$3p_1 - x$	$4d$	126151·6
2	1108·36	90223·1	206·2	$x - 4p_1$	x	258037·5
2	1110·90	90016·9		$x - 4p_2$		
0	1623·62	61590·7	210·7	$3d_2 - 4p_1$		
2	1624·00	61576·4		$3d_1 - 4p_1$		
2	1629·20	61380·0		$3d_2 - 4p_2$		
0	1739·03	57503·3	210·5	$4p_2 - 5s$		
1	1745·42	57292·8		$4p_1 - 5s$		
2	2387·72	41881·0	207·2	$4p_2 - 4d$		
3	2399·59	41673·8		$4p_1 - 4d$		
5	3098·36	32275·1	209·9	$4s - 4p_1$		
3	3118·65	32065·2		$4s - 4p_2$		

TABLE CXXXVI.

SERIES LINES OF Cl V.

Int.	λ I.A. (vac.).	ν.	Δν.	
3	538·08	185846·0	1456·4	$3p_2 - 3d$
4	542·33	184389·6		$3p_1 - 3d$
2	564·30	177210·7		
2	565·47	176844·0	1507·0	pp^* group
2	569·14	175703·7	1500·8	
2	570·31	175343·2		
6	629·33	158899·1		
6	633·18	157933·0	1495·6	pp^* group
6	635·31	157403·5	1497·3	
5	639·24	156435·7		

TABLE CXXXVII.

SCREENING CONSTANTS FOR REGULAR DOUBLETS, $3p_2 - 3p_1$.

	Δν.	$z - s$.	s_3.	s_2.	s_1.
Na .	—	—	—	—	7·450
Mg .	—	—	—	7·130	6·606
Al .	112·07	5·674	7·326	6·549	6·180
Si .	287·0	7·177	6·823	6·231	5·916
P .	559·5	8·481	6·519	6·042	5·741
S .	950·2	9·682	6·318	5·894	5·596
Cl .	1500·2	10·853	6·147	5·770	5·504

Millikan and Bowen [1] next deal with the phenomenon which underlies the groups of five lines in the spectra of the two-valency-electron systems and the groups of four lines in the case of the three-valency-electron systems. In the photographs of the spectra these groups are at once recognisable by their appearance, which is so characteristic that they serve as a means of identifying the two- and three-valency-electron systems, respectively.

The so-called pp^* group of lines in the spectra of calcium and strontium was first noted by Rydberg,[2] and in barium by Popow.[3] Götze [4] was the first to interpret these groups as being due to transitions from a new triplet p^* term to the normal triplet p term. As has already been explained this conclusion resulted from the fact that the inner quantum numbers of the two sets of triplet terms must be the same. The great theoretical interest of these multiplets lies in the fact that in calcium the values of the higher p^* terms were found to be less than zero. This was independently discovered by Wentzel [5] and by Russell and Saunders,[6] and leads to the very remarkable result that

[1] *Proc. Nat. Acad. Sci.*, **11**, 329 (1925); *Phys. Rev.*, **26**, 150 (1925).
[2] *Ann. der Phys.*, **52**, 119 (1924).
[3] *Ibid.*, **45**, 147 (1914). [4] *Ibid.*, **66**, 285 (1921).
[5] *Phys. Zeitsch.*, **24**, 106 (1923); **25**, 182 (1924).
[6] *Phys. Rev.*, **22**, 201 (1923).

in the transition from $6p^*$ to $4p$, for example, the energy radiated is larger than that radiated by the return of the electron from infinity to $4p$. Bohr suggested that the additional energy can only be obtained from the simultaneous jump of a second electron, the total energy change being just sufficient to give the observed wave-number. In other words, two electrons, both in unstable quantum states, simultaneously perform two definite quantum jumps and integrate these two into a single monochromatic radiation.

The first of these two electrons comes to rest in the lowest vacant p level. This is definitely known because certain lines of the six observed with calcium, magnesium, and beryllium show exactly the same separations as do the normal p levels, and these separations occur in such order as to show that the transitions take place to and not from these levels. In the second place, this first electron must jump from some triplet p term as established by the inner quantum number relations. In the third place, the second electron jumps to the lowest vacant s level. So much was known before Millikan and Bowen made their discovery. The initial level of the second electron was believed by Wentzel and by Russell and Saunders to be $3d$ in the case of calcium, but in the cases now under review this cannot be the case, though it may be correct for calcium. It may be noted that owing to want of sufficient resolving power Millikan and Bowen only found five lines instead of six in the case of their two-valency-electron systems.

In Table CXXXVIII. are set forth the wave-lengths and wave-numbers of the pp^* groups in the two series of two-valency-electron systems, Mg I. to Cl VI. and Be I. to O V., with the differences between the central and most intense lines.

The series of differences show how accurate is the linear progression of wave-number with atomic number. These pp^* groups therefore follow the irregular doublet law and hence the electron jumps must take place between levels of the same total quantum number. In the Be I. to O V. series the jumps are definitely limited to those between the $2s$ and $2p$ levels since there are no other levels with a total quantum number 2. This eliminates the suggestion made by Wentzel that the transition is $d \rightarrow s$, and also Landé's [1] proposal that the second electron jumps between orbits having different quantum numbers. As Millikan and Bowen say, the proof is complete and definite that the two electron jumps which combine to give the pp^* group in the Be I. to O V. series are (1) a jump of the first electron between two of the three levels, $2p_1$, $2p_2$, $2p_3$, and (2) a jump of the second electron from one of the $2p$ levels to the $2s$ level. Since the pp^* group has essentially the same structure in all two-valency-electron systems it is a natural inference that it always arises from these two jumps.

It would follow from this that the pp^* wave-numbers should be nearly the same as those of the $p \rightarrow s$ transition, *i.e.* the first member of the principal series of singlets, since the contribution made by the second jump is relatively small owing to the closeness of the p levels

[1] *Zeitsch. für Phys.*, **7**, 149 (1924).

TABLE CXXXVIII.

pp^* Groups in Two-Valency-Electron Systems.

	λ I.A. (vac.).	ν.	Diff.
	2777·503	36003·56	
	2779·084	35983·08	
Mg I.	2780·639	35962·96	
	2782·226	35942·44	
	2783·782	35922·35	
			20727·94
	1760·12	56814·3	
	1761·96	56755·0	
Al II.	1763·95	56690·9	
	1765·81	56631·2	
	1767·75	56569·1	
			20295·5
	1294·52	77248·7	
	1296·73	77117·1	
Si III.	1298·93	76986·4	
	1301·13	76856·3	
	1303·34	76726·0	
			20050·7
	1025·58	97506·0	
	1028·13	97264·2	
P IV.	1030·53	97037·1	
	1033·14	96792·4	
	1035·54	96567·9	
			19948·5
	849·25	117751·1	
	852·19	117345·0	
S V.	854·81	116985·6	
	857·83	116573·2	
	860·46	116216·9	
			19942·6
	724·13	138096·8	
	727·54	137449·5	
Cl VI.	730·31	136928·2	
	733·89	136260·2	
	736·76	135729·4	

	λ I.A. (vac.).	ν.	Diff.
	2651·343	37716·73	
	2651·438	37715·39	
Be I.	2651·507	37714·40	
	2651·585	37713·29	
	2651·652	37712·24	
			23858·8
	1623·66	61589·2	
	1623·86	61581·7	
B II.	1624·08	61573·2	
	1624·25	61567·0	
	1624·46	61558·9	
			23480·8
	1174·96	85109·0	
	1175·31	85084·2	
C III.	1175·72	85054·0	
	1176·03	85031·6	
	1176·40	85005·1	
			23267·2
	922·02	108457·5	
	922·57	108392·9	
N IV.	923·18	108321·2	
	923·68	108262·6	
	924·31	108188·8	
			23171·2
	758·76	131794·0	
	759·52	131662·1	
O V.	760·50	131492·4	
	761·21	131369·8	
	762·18	131202·6	

to one another. This is shown to be the case by the data given in Table CXXXIX. as closely as could be expected, in view of the fact that the P → S transition will not involve quite the same energy after a near-by electron has shifted its position as before that shift has taken place.

In order that a simultaneous two-electron jump can take place, it is necessary that both be at a given instant in a displaced position. In the present case the first electron must be in one of the $2p$ levels at the same time as the second electron is in some $2p$ level. If these two displacements are not the result of a single act, the first electron must be held in a metastable position until another act can displace the second electron. The $2p_1$ and $2p_3$ levels are metastable, but the $2p_2$ level is definitely not so. Now the approximate equality in the intensities of the pp^* lines shows that all of the three $2p_{1,2,3}$ levels are

TABLE CXXXIX.

COMPARISON OF WAVE-NUMBERS OF *pp** GROUP WITH (3S – 3P) JUMP.

	3S – 3P.	*pp**.
Mg I. . .	35051·4	35962·96
Al II. . .	59845·1	56690·9
Si III. . .	82878·9	76986·4
P IV. . .	105190·4	97037·1
S V. . .	127144·0	116985·6
Cl VI. . .	148949·2	136928·2
Ca I. . .	23652·4	23254·66
Sr I. . .	21698·4	20895·5
Ba I. . .	18060·2	10843·5

equally metastable, *i.e.* they are equally likely to be the seat of one of the two jumping electrons, when the double jump occurs. Millikan and Bowen, therefore, conclude that it is one single act that displaces two electrons from the *s* level to the two *p* levels, from which they jump simultaneously to give the *pp** group.

Turning next to the three-valency-electron systems, Millikan and Bowen concluded that *pp** groups must also be present in their spectra and that they must be quadruplets instead of sextuplets. They were the first to discover these since this group in general lies in the extreme ultra-violet. We have already recorded their existence in Tables CXXXIV. to CXXXVI. and they are set forth with the differences in Table CXL.

TABLE CXL.

*pp** GROUPS IN THE THREE-VALENCY-ELECTRON SYSTEMS.

	λ I.A. (vac.).	ν.	Diff.
	903·63	110664·8	
	903·98	110621·9	
C II.	904·17	110598·7	
	904·48	110560·8	
			35203·7
	685·04	145976·9	
N III.	685·55	145868·4	
	685·86	145802·4	
	686·39	145689·8	
			34533·7
	553·33	180724·0	
O IV.	554·07	180482·6	
	554·52	180336·1	
	555·23	180105·5	

	λ I.A. (vac.).	ν.	Diff.
	1762·79	56728·3	
	Obscured.		
Al I.	1766·31	56615·2	
	1768·95	56530·9	
			27101·8
	1190·42	84004·0	
Si II.	1193·31	83800·5	
	1194·50	83717·0	
	1197·42	83512·9	
			25133·9
	913·99	109410·7	
P III.	917·14	109035·2	
	918·69	108850·9	
	921·86	108476·0	
			24441·4
	744·92	134242·8	
S IV.	748·40	133618·6	
	750·23	133292·3	
	753·76	132668·6	
			24111·2
	629·33	158800·1	
Cl V.	633·18	157933·0	
	635·31	157403·5	
	639·24	156435·7	

There is no question that this work by Millikan and Bowen is of very great importance and no apology is needed for the following quotations from their paper.

In the three-valency-electron system it is known from absorption experiments in aluminium vapour, for example, that in the normal state two of the valency electrons are in the $3s$ level and the third in a $3p$ level. About these three occupied outer orbits (levels) are then arranged the series of virtual orbits in jumping between which the third electron produces the ordinary series of arc lines. This series of orbits is diagrammatically represented by the continuous lines in Fig. 28. When, now, one of the $3s$ electrons absorbs energy and is thus elevated to a $3p$ orbit, its removal from the s level changes the field strength everywhere about the nucleus so that the new series of virtual orbits is now in displaced positions, as represented by the dotted lines. These new orbits are designated as $3p_1^*$, $3p_2^*$, etc.

When, now, one of the two electrons in a p position jumps back to the vacant s position the $3p^*$ levels cease at once to exist, the $3p_1$, $3p_2$, etc., positions re-appearing instantly. Hence, a jump of one electron from a $3p$ to a $3s$ position is necessarily accompanied by a

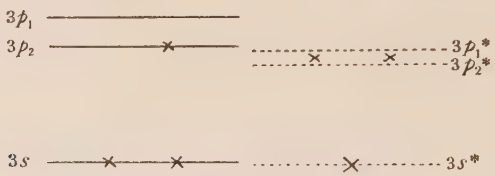


FIG. 28.

shift of the other $3p$ electrons form a $3p^*$ level to a $3p$ level. But when this shift takes place the existence of four lines in the pp^* group shows that the electron which is forced out of a $3p^*$ orbit by the jerking of that orbit out from under it, so to speak, may make the shift to a $3p$ orbit in four different ways: by changing (1) from $3p_1^*$ to $3p_1$ or (2) from $3p_2^*$ to $3p_2$ without change in inner quantum number, or (3) from $3p_1^*$ to $3p_2$ or (4) from $3p_2^*$ to $3p_1$ with change in inner quantum number. The two central lines of the quadruplet pp^* group correspond to the first and second of these changes, the two outer lines to the third and fourth. The fact that the two central lines are not coincident shows that the energy change from $3p_1^*$ to $3p_1$ is not quite the same as from $3p_2^*$ to $3p_2$. This is to be expected from the difference in the fields in which the p and the p^* orbits lie in virtue of the change of position of an s electron.

The fundamental significance of the two electron jumps lies in the new light which they throw upon the problem of the relation between the energy of ether waves (radiant energy) and atomic or sub-atomic energy (material energy).

These experiments constitute new proof of the futility of the nineteenth-century attempt to find the origin of monochromatic ether

waves in the vibratory motion of charged particles of any sort. Within the last ten years, an atom or molecule has been definitely shown, first by relationships discovered in band spectra,[1] and second by two-electron jumps of the sort now discussed, to have the capacity of integrating any sort of a complex sub-atomic or sub-molecular shudder into a monochromatic ether wave, the frequency ν of which is determined by $h\nu = E_1 - E_2$, E_1 and E_2 representing the total energy before and after the shudder respectively. The facts of band spectra show that this integrating process can combine into one emitted frequency a change (1) in the energy of rotation of the two nuclei of a diatomic dumb-bell shaped molecule, (2) in the vibration of these two nuclei along their line of connection, or (3) in the kinetic or potential energy of one of the electronic constituents of the system.

These results, together with those of Wentzel and of Russell and Saunders, which they supplement, prove conclusively that two electrons may simultaneously change their energies within an atom

TABLE CXLI.

SERIES LINES OF B II.

Int.	λ I.A. (vac.).	ν.	Δν.		Term values.	
0	731·46	136712·9		$2p - 4d$	$3s$	72930·8
3	882·55	113308·2	18·3	$2p_{2,3} - 3d$	$4s$	36655·5
3	882·69	113289·9		$2p_1 - 3d$	$2p_1$	165343·9
					$2p_{2,3}$	165362·7
3	1081·88	92432·1	19·3	$2p_{2,3} - 3s$		
					$3p_1$	59006·5
3	1082·10	92412·8		$2p_1 - 3s$	$3p_{2,3}$	59010·0
8	1362·46	73396·5		2S — 2P	$3d$	52054·2
4	1623·66	61589·2			$4d$	28640·4
4	1623·86	61581·7				
5	1624·08	61573·2		pp^* group	$4f$	27800·0
4	1624·25	61567·0				
4	1624·46	61558·9			$5f$	17795·7
5	1842·83	54264·3		2P — 3S	2S	194325·9
2	2918·98	34258·5		$3d - 5f$	3S	66665·1
10	3452·33	28965·9		2S — $2p_{2,3}$	2P	120929·4
6	4122·99	24254·2		$3d - 4f$	3D	48410·3
1	4473·37	22354·5	3·5	$3p_{2,3} - 4s$		
1	4474·08	22351·0		$3p_1 - 4s$		

[1] See Chap. IV.

and integrate their joint energy change into an emitted monochromatic ether wave. The mechanism by which such an integration takes place is thus far a complete mystery. We are here in the presence of one of the ultimate phenomena of the physical world. The contribution of the present experiments to the understanding of these phenomena consists simply (1) in the proof which they furnish that the particular two-electron jumps which are here integrated are (*a*) a jump of one electron from a *p* to an *s* position, and (*b*) a simultaneous jump of another electron from one *p* position to another *p* position, (2) in the evidence which they bring to light that every one of a long series of two-valency-electron systems is characterised by essentially the same sort of an easily recognisable sextuplet pp^* group, this sextuplet appearing without essential modification in such different two-valency-electron systems as Be I. to O V. and Mg I. to Cl VI., (3) in the discovery that a three-valency-electron system is similarly characterised by a quadruplet pp^* group which is found in all the three-valency-electron systems studied, (4) in the proof that the variation of the frequency of pp^* groups with atomic number follows the irregular doublet law and hence that the group is formed by jumps between levels of the same total quantum number.

In concluding this account of Millikan and Bowen's investigations, the series data are given in Tables CXLI. and CXLII. of the spectra of the two-valency-electron systems of B II. and C III.[1]

TABLE CXLII.

SERIES LINES OF C III.

Int.	λ I.A. (vac.).	ν.	Δν.		Term values.	
6	459·7	217552		$2p - 3d$	$3s$	146197·2
7	538·4	185742		$2p - 3s$	$2p$	331939·2
12	977·02	102352·1		2S − 2P	$3p_1$	124685·8
					$3p_2$	124698·6
4	1174·96	85109·0			$3p_3$	124704·1
4	1175·31	85084·2				
5	1175·72	85054·0		pp^* group	$3d$	114387·2
4	1176·03	85031·6				
4	1176·40	85005·1			$4f$	62600
7	1930·98	51787·2		$3d - 4f$	2S	375463·1
10	2297·59	43523·9		2S − $2p_2$	2P	273111·0
3	4648·70	21511·4	12·8	$3s - 3p_1$		
2	4651·46	21498·6		$3s - 3p_2$		
1	4652·65	21493·1	5·5	$3s - 3p_3$		

[1] *Phys. Rev.*, **26**, 310 (1925).

Lastly, we may add Table CXLIII. for the sake of exhibiting even more strikingly than has been done before, first, the systematic progression of the screening constant of the regular doublet law as each new electron is added to the valency shell, and second, the fact that the triplets behave precisely as do the doublets in systems of like electronic structure and varying nuclear charge. The upper half of the table gives the $(2p_2 - 2p_1)$ doublet separations in the first, third and fifth columns for one-, three-, and five-electron systems, respectively, and the $(2p_3 - 2p_1)$ triplet separations in the second, fourth, and sixth columns, for two-, four-, and six-electron systems. For the two-valency-electron systems these separations are obtained from the pp^* groups. The lower half of the table gives the values of the screening constant as computed from the regular doublet law. The table shows very clearly the effect upon the force field about the nucleus of the successive addition up to six of each new valency electron to the valency shell. The progression is at least qualitatively in agreement with that to be expected from the successive introduction into the atom of six point charges each endowed with a coulomb field.

TABLE CLXIII.

FREQUENCY SEPARATIONS AND SCREENING CONSTANTS FOR REGULAR DOUBLETS AND TRIPLETS.

Electrons.	1. $2p_2 - 2p_1$.	2. $2p_3 - 2p_1$.	3. $2p_2 - 2p_1$.	4. $2p_3 - 2p_1$.	5. $2p_2 - 2p_1$.	6. $2p_3 - 2p_1$.
Li	0·338					
Be	6·61	3·02				
B	34·1	22·8	15·55			
C	107·4	79·1	66·76	46·8		
N	259·1	204·1	179·3	132·2	85·3	
O		459·5	398·4	309·0		224·0

Screening Constant, $s = Z - \sqrt[4]{\Delta\nu/0{\cdot}365}$.

Li	2·019				
Be	1·937	2·304			
B	1·884	2·189	2·445		
C	1·858	2·163	2·332	2·635	
N	1·838	2·137	2·292	2·638	3·090	
O		2 043	2·252	2·606		3·023

The Second Type of Regularity in Spectra.- Under this title there have been grouped a number of spectra in which series of the type we have principally been concerned with have not as yet been recognised. In these spectra a different type of regularity was discovered by Kayser [1] and by Kayser and Runge.[2] The regularity consists in the recurrence of certain constant wave-number differences, and this may be instanced by tin and antimony which were examined by Kayser and Runge. In Table CXLIV. are shown certain groups of constant wave-number difference in the spectrum of tin.

[1] *Abh. d. Berl. Akad.*, 1897. [2] *Ibid.*, 1894.

TABLE CXLIV.

TIN.

1.	2.	3.	4.	5.
λ.	λ.	Diff.	λ.	Diff.
3801·16	3175·13	− 0·01	3009·24	0·00
3330·71	2840·05	+ 0·01	2706·59	+ 0·02
2850·72	2483·49	+ 0·01	2380·83	− 0·01
2813·66	2455·32	− 0·02	2354·93	+ 0·01
2785·14	2433·57	− 0·04	2334·93	− 0·04
2779·92	2429·59	− 0·01	—	—
2594·49	2286·75	+ 0·04	2199·42	+ 0·04
2571·67	2269·00	+ 0·03	—	—
2524·05	2231·85	+ 0·05	2148·59	+ 0·11
2495·80	2209·73	+ 0·05	—	—
2408·27	2140·84	+ 0·26	2064·12	− 0·32
2359·05	2101·06	− 0·16	—	—
2317·32	2068·67	+ 0·03	—	—

In this table the first column contains a number of lines, the wave-numbers of which when increased by 5187·03 give the lines in the second column, the errors being shown in column 3; again, if we add 6923·26 to the wave-numbers of the lines in the first column, the wave-numbers of the lines in the fourth column are obtained with the differences given in the fifth column. In this way the lines in the horizontal rows form triplets of constant wave-number difference.

A similar arrangement was found in the case of antimony, as shown in Table CXLV.

TABLE CXLV.

ANTIMONY.

1.	2.	3.	4.	5.	6.
4033·70	3722·92	—	—	—	—
3637·94	3383·23	2770·03	2670·73	2395·30	2352·32
3232·61	3029·91	2528·61	2445·61	2212·63	2175·90
2851·20	2962·34	2289·09	2220·85	—	
2719·00	2574·15	2203·09	2139·81	—	—
2652·70	2514·65	2159·36	2098·53	—	—
2614·74	2480·51	—	—	—	—
2554·72	2426·44	—	—	—	—
2481·81	2360·57	—	—	—	—
2373·78	2262·63	—	—	—	—
2329·19	2222·08	—	—	—	—
2306·56	2201·47	—	—	—	—

The number of elements showing this type of spectrum has largely been extended by Paulson.[1]

[1] *Astrophys. Journ.*, **40**, 298 (1914); **41**, 72 (1915); *Phys. Zeitsch.*, **15**, 892 (1914); **16**, 7, 81, 352 (1915); **19**, 13 (1918); *Ann. der Phys.*, **45**, 1203 (1914); **46**, 698 (1915); *Zeitsch. wiss. Phot.*, **18**, 202 (1919).

This type of regularity was generally accepted as being essentially different from the ordinary series type, but the enunciation of the combination principle by Ritz suggested at once that these spectra are composed of a great number of combination lines without any series of the normal type being present. This suggestion, however, did not do more than indicate an abnormal number of terms with a corresponding complexity of combinations. Some considerable light has been thrown on the problem by Paschen's work on neon which has already been described. It must be remembered that the earlier work on this spectrum had shown some indications that it was analogous to those of our second type. It had been pointed out by Watson [1] that many of the strong lines could be arranged in quadruplets with constant wave-number separations, and it was further noted by Rossi [2] that two sets of doublet series could be traced. The solution of this particular spectrum was found by Paschen who succeeded in proving the presence of 130 series which are closely related. The details of this structure were given on p. 218, the chief characteristic being the great number of spectral terms. There are four series of *s* terms, ten series of *p* terms, and twelve series of *d* terms. There thus could theoretically exist forty sharp series, forty principal series, and 120 diffuse series, or 200 series in all.

As was explained on p. 212 it was Paschen's work which led Landé to put forward his scheme of multiplicities of higher orders of complexity based on Heisenberg's conception of the branching of terms, each branching consisting of a single term giving two terms with $I \rightarrow I \pm 1/2$. Then, again, there is the more recent theory of Heisenberg, which has been applied by Fowler and Hartree to the spectrum of O II. (p. 228). There is little doubt that the secret of the spectra of the second type of regularity will be found in the fact that the multiplicity of their spectral terms is of the second, or possibly of a still higher, order of complexity. Further work on these spectra is very urgently needed.

Allocation of Lines in Series.—Although a valuable indication of a general method of procedure is to be found in Fowler's work [3] on the spectral series of silicon and oxygen, and in Catalan's work [4] on the spectra of manganese, we may consider this problem in greater detail. In the first place, it may be noted that the lines belonging to the same series exhibit in general the same physical characteristics as regards sharpness, etc., and they also show decreasing intensity as their wave-numbers increase. These two facts form a valuable guide at the outset, since it is often possible from an inspection of a photograph of a spectrum to pick out the lines which belong to a series. It is convenient also to construct a map of the spectrum in which the lines are distributed according to their wave-numbers, and their intensities indicated by their lengths. When a number of lines have

[1] *Astrophys. Journ.*, **33**, 399 (1911).
[2] *Phil. Mag.*, **26**, 981 (1913).
[3] See pp. 81 and 223.
[4] See p. 119.

TABLE CXLVI.

μ.	$m=1$.	Diff.	$m=2$.	Diff.	$m=3$.	Diff.	$m=4$.	Diff.	$m=5$.	Diff.	$m=6$.	Diff.	$m=7$.	Diff.	$m=8$.	Diff.	$m=9$.	μ.
0·00	109678	82258	27420	15233	12187	5332	6855	2468	4387	1340	3047	809	2238	524	1714	360	1354	0·00
0·01	107517	80370	27147	15041	12106	5285	6821	2451	4370	1333	3037	805	2232	523	1709	358	1351	0·01
0·02	105419	78540	26879	14853	12026	5239	6787	2435	4352	1326	3026	801	2225	520	1705	357	1348	0·02
0·03	103382	76767	26615	14669	11946	5193	6753	2418	4335	1319	3016	797	2219	518	1701	356	1345	0·03
0·04	101404	75049	26355	14487	11868	5148	6720	2402	4318	1312	3006	793	2213	516	1697	355	1342	0·04
0·05	99481	73383	26098	14308	11790	5103	6687	2386	4301	1304	2997	790	2207	514	1693	354	1339	0·05
0·06	97613	71767	25846	14133	11713	5059	6654	2370	4284	1297	2987	787	2200	512	1688	352	1336	0·06
0·07	95797	70200	25597	13960	11637	5016	6621	2354	4267	1290	2977	783	2194	510	1684	351	1333	0·07
0·08	94031	68680	25351	13789	11562	4973	6589	2339	4250	1283	2967	779	2188	508	1680	350	1330	0·08
0·09	92314	67205	25109	13622	11487	4930	6557	2324	4233	1276	2957	775	2182	506	1676	349	1327	0·09
0·10	90643	65773	24870	13457	11413	4888	6525	2308	4217	1269	2948	772	2176	504	1672	347	1325	0·10
0·11	89017	64382	24635	13296	11339	4847	6492	2292	4200	1262	2938	768	2170	502	1668	346	1322	0·11
0·12	87435	63032	24403	13136	11267	4806	6461	2277	4184	1256	2928	765	2163	500	1663	344	1319	0·12
0·13	85894	61719	24175	12980	11195	4765	6430	2262	4168	1249	2919	762	2157	498	1659	343	1316	0·13
0·14	84394	60445	23949	12825	11124	4725	6399	2248	4151	1242	2909	758	2151	496	1655	342	1313	0·14
0·15	82933	59206	23727	12674	11053	4685	6368	2233	4135	1235	2900	755	2145	494	1651	341	1310	0·15
0·16	81509	58001	23508	12524	10984	4646	6338	2219	4119	1228	2891	752	2139	492	1647	340	1307	0·16
0·17	80122	56830	23292	12377	10915	4608	6307	2204	4103	1222	2881	748	2133	490	1643	339	1304	0·17
0·18	78769	55691	23078	12232	10846	4569	6277	2189	4088	1216	2872	744	2128	489	1639	337	1302	0·18
0·19	77451	54583	22868	12090	10778	4531	6247	2175	4072	1209	2863	741	2122	487	1635	336	1299	0·19
0·20	76166	53505	22661	11950	10711	4494	6217	2161	4056	1203	2853	737	2116	485	1631	335	1296	0·20
0·21	74912	52456	22456	11812	10644	4456	6188	2147	4041	1197	2844	734	2110	483	1627	334	1293	0·21
0·22	73689	51435	22254	11676	10578	4419	6159	2134	4025	1190	2835	731	2104	481	1623	333	1290	0·22
0·23	72495	50440	22055	11542	10513	4383	6130	2120	4010	1184	2826	728	2098	479	1619	332	1287	0·23
0·24	71331	49472	21859	11411	10448	4347	6101	2107	3994	1177	2817	725	2092	477	1615	331	1284	0·24

0·25	70194	48529	21665	11281	10384	4312	6072	2093	3979	1171	2808	721	2087	475	1612	330	1282	0·25
0·26	69084	47611	21473	11153	10320	4276	6044	2080	3964	1165	2799	718	2081	473	1608	329	1279	0·26
0·27	68001	46716	21285	11028	10257	4242	6015	2066	3949	1159	2790	715	2075	471	1604	328	1276	0·27
0·28	66942	45844	21098	10903	10195	4208	5987	2053	3934	1153	2781	712	2069	469	1600	326	1274	0·28
0·29	65909	44994	20915	10782	10133	4174	5959	2040	3919	1147	2772	708	2064	468	1596	325	1271	0·29
0·30	64898	44165	20733	10662	10071	4139	5932	2028	3904	1141	2763	705	2058	466	1592	324	1268	0·30
0·31	63911	43357	20554	10543	10011	4106	5905	2015	3890	1135	2755	702	2053	465	1588	323	1265	0·31
0·32	62947	42570	20377	10427	9950	4073	5877	2002	3875	1129	2746	699	2047	463	1584	322	1263	0·32
0·33	62004	41801	20203	10312	9891	4041	5850	1989	3861	1124	2737	696	2041	461	1581	321	1260	0·33
0·34	61086	41055	20031	10199	9832	4009	5823	1977	3846	1117	2729	693	2036	459	1577	320	1257	0·34
0·35	60180	40320	19860	10087	9773	3977	5796	1964	3832	1112	2720	690	2030	457	1573	319	1254	0·35
0·36	59298	39606	19692	9977	9715	3945	5770	1952	3818	1106	2712	687	2025	455	1570	318	1252	0·36
0·37	58436	38910	19526	9869	9657	3914	5743	1940	3803	1100	2703	684	2019	453	1566	317	1249	0·37
0·38	57592	38229	19363	9763	9600	3883	5717	1928	3789	1094	2695	681	2014	452	1562	315	1247	0·38
0·39	56766	37564	19202	9658	9544	3853	5691	1916	3775	1088	2686	678	2008	450	1558	314	1244	0·39
0·40	55958	36916	19042	9554	9488	3823	5665	1904	3761	1083	2678	675	2003	449	1554	313	1241	0·40
0·41	55167	36283	18884	9452	9432	3793	5639	1892	3747	1078	2669	672	1997	447	1550	312	1238	0·41
0·42	54393	35665	18728	9351	9377	3763	5614	1880	3734	1073	2661	669	1992	445	1547	311	1236	0·42
0·43	53635	35061	18574	9252	9322	3733	5589	1869	3720	1067	2653	666	1987	444	1543	310	1233	0·43
0·44	52893	34471	18422	9154	9268	3704	5564	1857	3707	1062	2645	663	1982	442	1540	309	1231	0·44
0·45	52166	33894	18272	9057	9215	3676	5539	1846	3693	1057	2636	660	1976	440	1536	308	1228	0·45
0·46	51454	33330	18124	8962	9162	3648	5514	1835	3679	1051	2628	658	1970	438	1532	307	1225	0·46
0·47	50756	32778	17978	8869	9109	3620	5489	1823	3666	1046	2620	655	1965	436	1529	306	1223	0·47
0·48	50072	32239	17833	8776	9057	3592	5465	1812	3653	1041	2612	652	1960	435	1525	305	1220	0·48
0·49	49402	31712	17690	8685	9005	3565	5440	1801	3639	1035	2604	649	1955	433	1522	304	1218	0·49

TABLE CXLVI.—*Continued.*

μ.	$m=1$.	Diff.	$m=2$.	Diff.	$m=3$.	Diff.	$m=4$.	Diff.	$m=5$.	Diff.	$m=6$.	Diff.	$m=7$.	Diff.	$m=8$.	Diff.	$m=9$.	μ.
0·50	48746	31197	17549	8596	8953	3537	5416	1790	3626	1030	2596	646	1950	432	1518	303	1215	0·50
0·51	48102	30693	17409	8507	8902	3510	5392	1779	3613	1025	2588	643	1945	430	1515	302	1213	0·51
0·52	47472	30201	17271	8419	8852	3484	5368	1769	3599	1019	2580	641	1939	428	1511	301	1210	0·52
0·53	46854	29719	17135	8333	8803	3457	5345	1759	3586	1014	2572	638	1934	427	1507	300	1207	0·53
0·54	46247	29247	17000	8248	8752	3431	5321	1748	3573	1009	2564	635	1929	425	1504	299	1205	0·54
0·55	45652	28785	16867	8164	8703	3405	5298	1737	3561	1004	2557	633	1924	424	1500	298	1202	0·55
0·56	45068	28332	16736	8082	8654	3379	5275	1727	3548	999	2549	630	1919	422	1497	297	1200	0·56
0·57	44496	27890	16606	8000	8606	3354	5252	1717	3535	994	2541	627	1914	421	1493	296	1197	0·57
0·58	43935	27458	16477	7919	8558	3329	5229	1707	3522	989	2533	624	1909	419	1490	295	1195	0·58
0·59	43384	27034	16350	7840	8510	3304	5206	1696	3510	984	2526	622	1904	418	1486	294	1192	0·59
0·60	42843	26618	16225	7762	8463	3280	5183	1686	3497	979	2518	619	1899	416	1483	293	1190	0·60
0·61	42313	26212	16101	7685	8416	3255	5161	1676	3485	975	2510	616	1894	414	1480	292	1188	0·61
0·62	41792	25814	15978	7608	8370	3231	5139	1666	3473	970	2503	614	1889	413	1476	291	1185	0·62
0·63	41281	25424	15857	7533	8324	3208	5116	1656	3460	965	2495	611	1884	411	1473	290	1183	0·63
0·64	40779	25042	15737	7459	8278	3184	5094	1646	3448	961	2487	608	1879	410	1469	289	1180	0·64
0·65	40286	24668	15618	7385	8233	3161	5072	1636	3436	956	2480	606	1874	408	1466	288	1178	0·65
0·66	39802	24301	15501	7313	8188	3137	5051	1627	3424	951	2473	604	1869	407	1462	287	1175	0·66
0·67	39327	23942	15385	7242	8143	3114	5029	1617	3412	947	2465	601	1864	405	1459	286	1173	0·67
0·68	38860	23589	15271	7172	8099	3091	5008	1608	3400	942	2458	598	1860	404	1456	285	1171	0·68
0·69	38401	23244	15157	7102	8055	3069	4986	1598	3388	937	2451	596	1855	403	1452	284	1168	0·69
0·70	37951	22906	15045	7034	8011	3046	4965	1589	3376	933	2443	593	1850	401	1449	283	1166	0·70
0·71	37508	22574	14934	6966	7968	3024	4944	1580	3364	928	2436	591	1845	400	1445	282	1163	0·71
0·72	37074	22249	14825	6899	7926	3003	4923	1571	3352	923	2429	589	1840	398	1442	281	1161	0·72
0·73	36646	21930	14716	6833	7883	2981	4902	1562	3340	918	2422	586	1836	397	1439	280	1159	0·73
0·74	36226	21617	14609	6768	7841	2959	4882	1553	3329	915	2414	583	1831	395	1436	280	1156	0·74

0·75	35813	21310	14503	6704	7799	2938	4861	1544	3317	910	2407	581	1826	393	1433	279	1154	0·75
0·76	35408	21010	14398	6640	7758	2917	4841	1535	3306	906	2400	579	1821	392	1429	278	1151	0·76
0·77	35009	20815	14294	6577	7717	2897	4820	1526	3294	901	2393	576	1817	391	1426	277	1149	0·77
0·78	34616	20424	14192	6516	7676	2876	4800	1517	3283	897	2386	574	1812	389	1423	276	1147	0·78
0·79	34231	20141	14090	6454	7636	2856	4780	1508	3272	893	2379	572	1807	388	1419	275	1144	0·79
0·80	33851	19861	13990	6394	7596	2836	4760	1500	3260	888	2372	569	1803	387	1416	274	1142	0·80
0·81	33478	19588	13890	6334	7556	2815	4741	1492	3249	884	2365	567	1798	385	1413	273	1140	0·81
0·82	33111	19319	13792	6276	7516	2795	4721	1483	3238	880	2358	564	1794	384	1410	273	1137	0·82
0·83	32751	19056	13695	6218	7477	2776	4701	1474	3227	876	2351	562	1789	382	1407	272	1135	0·83
0·84	32396	18798	13598	6160	7438	2756	4682	1466	3216	872	2344	560	1784	380	1404	271	1133	0·84
0·85	32046	18543	13503	6104	7399	2736	4663	1458	3205	868	2337	557	1780	379	1401	270	1131	0·85
0·86	31703	18294	13409	6048	7361	2717	4644	1450	3194	864	2330	555	1775	378	1397	269	1128	0·86
0·87	31364	18048	13316	5993	7323	2698	4625	1442	3183	859	2324	553	1771	377	1394	268	1126	0·87
0·88	31032	17809	13223	5938	7285	2679	4606	1434	3172	855	2317	551	1766	375	1391	267	1124	0·88
0·89	30704	17572	13132	5884	7248	2661	4587	1425	3162	851	2311	549	1762	374	1388	267	1121	0·89
0·90	30382	17340	13042	5831	7211	2643	4568	1417	3151	847	2304	547	1757	372	1385	266	1119	0·90
0·91	30065	17113	12952	5778	7174	2625	4549	1409	3140	843	2297	544	1753	371	1382	265	1117	0·91
0·92	29752	16889	12863	5725	7138	2607	4531	1402	3129	839	2290	541	1749	370	1379	264	1115	0·92
0·93	29445	16669	12776	5674	7102	2589	4513	1394	3119	835	2284	540	1744	369	1375	263	1112	0·93
0·94	29142	16453	12689	5624	7065	2571	4494	1386	3108	831	2277	537	1740	368	1372	262	1110	0·94
0·95	28844	16241	12603	5573	7030	2554	4476	1378	3098	827	2271	535	1736	367	1369	261	1108	0·95
0·96	28550	16032	12518	5524	6994	2536	4458	1370	3088	824	2264	533	1731	365	1366	260	1106	0·96
0·97	28261	15827	12434	5475	6959	2519	4440	1363	3077	820	2258	531	1727	364	1363	260	1103	0·97
0·98	27976	15625	12351	5427	6924	2501	4423	1356	3067	816	2251	529	1722	362	1360	259	1101	0·98
0·99	27696	15428	12268	5379	6889	2484	4405	1348	3057	812	2245	527	1718	361	1357	258	1099	0·99
1·00	27420	15233	12187	5332	6855	2468	4387	1340	3047	809	2238	524	1714	360	1354	257	1097	1·00

been selected as belonging to a number of series, their wave-numbers may be plotted against consecutive integers and the regularity of the curve thus drawn affords a valuable indication as to the correctness of the allocation.

Although the Rydberg formula is not sufficiently exact to represent the wave-numbers of a series accurately, yet it is extremely useful in the preliminary stages of the work. The most convenient method of utilising this formula is by means of an interpolation table such as was described on p. 11. This table renders invaluable aid both in selecting the lines of a series and in finding an approximate value for the convergence limit of that series. As was stated previously Rydberg published an interpolation table for use with his formula, this table containing the values of $N/(m + \mu)^2$ for $m = 1, 2, 3, \ldots 9$ and $\mu = 0{\cdot}01, 0{\cdot}02, 0{\cdot}03 \ldots 1{\cdot}00$. This table had been calculated with $N = 109721{\cdot}6$, which was obtained from the earlier measurements of the hydrogen lines. Since the value of 109678·3 has now been adopted for N, the table has been re-calculated and may be reproduced here on account of its extreme usefulness [1] (see p. 300).

The method of using this table may be indicated. Let it be supposed that two lines have been found which, owing to their similarity seem to be consecutive members of the same series and which have the wave-numbers 30926 and 36468. The difference in wave-number is 5542 and from the table we find that

$$5573 = \frac{N}{(2{\cdot}95)^2} - \frac{N}{(3{\cdot}95)^2} = 12603 - 7030$$

and

$$5524 = \frac{N}{(2{\cdot}96)^2} - \frac{N}{(3{\cdot}96)^2} = 12518 - 6994.$$

By interpolation we find that

$$5542 = \frac{N}{(2{\cdot}95633)^2} - \frac{N}{(3{\cdot}95633)^2} = 12549 - 7007.$$

It follows from this that the convergence limit is given by

$$A = 30926 + 12549 = 43475,$$

or

$$A = 36468 + 7007 = 43475,$$

and hence the equation for the series is

$$\nu = 43475 - \frac{N}{(m + 0{\cdot}95633)^2}.$$

With the help of this equation the approximate wave-numbers of the other lines of the series can be calculated and these lines can at once be sought for in the spectrum. If found, all doubt will vanish as

[1] See also Fowler's *Report on Series in Line Spectra*, p. 82.

to the reality of the series, and from their true wave-numbers the series constants may be accurately calculated by means of the Ritz or Hicks formula. In order to show the accuracy obtainable, it may be said that the two lines selected above are two members of the principal series of lithium. The true value of the convergence limit of this series is 43486·3, which is very near to the approximate value calculated above.

In the case of enhanced line spectra, it must be remembered that the Rydberg series term is of the type $x^2N/(m+\mu)^2$, where $x = 2, 3, 4$, etc. In using the interpolation table therefore in work on enhanced series it will be necessary first to divide the value of Δn by 4, 9, 16, etc., according to the conditions of ionisation present. The values of $N/(m+\mu)^2$ must then be multiplied by 4, 9, 16, etc., in order to find the limit of the series. As an example we may take two of the lines of Si IV. with wave-numbers 43710 and 65212, the value of Δn being 21502.

Now $21502/16 = 1344$, and from the interpolation table we find that

$$1344 = \frac{N}{(4\cdot955)^2} - \frac{N}{(5\cdot995)^2} = 4396 - 3052.$$

The convergence limit is given by

$$4396 \times 16 + 43710 = 114046,$$

and

$$3052 \times 16 + 65212 = 114044.$$

The Rydberg formula for the series is therefore

$$n = 114045 - \frac{16N}{(m + 0\cdot995)^2} \text{ where } m = 4, 5, \text{ etc.}$$

The convergence limit found by Fowler as shown in the table on p. 87 is 114076.

Although it might appear at first sight that the value of m in Rydberg's formula is of little importance, since we find from the table and make use of the value of $m + \mu$, this is by no means the case. From what has already been said in connection with the relations between the four series, it is essential that the true value of m be known in order to establish the four series in correct orientation with one another. The first fact to be remembered is that the first members of the principal and sharp series have the same separations, and hence the numeration must be such that $P(1) = -S(1)$. The same is true of course for singlet series. As was mentioned on p. 36 the sign is reversed in the case of some elements such as the aluminium sub-group where $S(1) = -P(1)$. The numeration of the lines must be such that $m = 1$ in the true first members of both the sharp and principal series. Thus in the case of sodium the constant separation of the sharp doublets is 17·18 and this is the separation of the D lines, which thus must form the first principal pair with $m = 1$.

The wave-numbers of the first two less refrangible members of the principal pair series of sodium are 16973 and 30273, the difference being 13300. From the interpolation table this difference is given very approximately by

$$n = \frac{N}{(2{\cdot}11)^2} - \frac{N}{(3{\cdot}11)^2}.$$

Since, however, $m = 1$ for the first line, $\mu = 1{\cdot}11$.

There is no such criterion for the diffuse series and, in view of the fact that the sharp and diffuse series have the same convergence limit, it is customary to give the same value of m to neighbouring lines in the two series. As already explained, $m = 2$ for the first member of the diffuse series in most cases. When satellites are present, then information may be gained at once as to the true first member of the diffuse series from the fact that the satellite separation in that member will equal the separation between the components of the fundamental series.

The most important factors to be considered in correlating together lines which belong to the same series are their physical characteristics, and in particular the Zeeman effect. The information that is gained from a knowledge of the resolution of a spectrum line in the magnetic field is of paramount importance. Not only does the type of resolution remain constant in any given series, but, as the result of the more recent advances in that field, it is possible from a knowledge of the separation of the components of the resolution picture to assign any line to its series and to its system (doublet, triplet, quartet, etc.). As has already been emphasised, the more recent advances in the two fields, spectral series and Zeeman effect, have been closely associated, the two in the end forming a unified whole. This statement will be better understood from the account of the latest work on the Zeeman effect, which must, however, be postponed till Chapter II.

In concluding this account of spectral series, which can at best only be viewed as a guide to those who wish to understand the progress made during the last twelve years, a few words may be said with respect to the labours of the investigators in new fields of series relationships. Whilst some indication may have been given of the methods in the account of the work of Fowler, Catalan, Millikan and Bowen, and others, the fields yet unexplored promise to be beset with great difficulties. In this respect reference may be made to a recent paper by Carroll [1] on the vacuum spark spectra of Hg II., Ga III., In III., Tl III., Ge IV., Sn IV., and Pb IV, wherein he points out the great difference between the problem of identifying the series lines in these spectra, and that of arranging the lines in ordinary arc and spark spectra. The outstanding guides, such as Zeeman effect, temperature classification, reversal, ionisation or resonance potentials, were not to hand, nor did the lines show any well-marked differences

[1] *Phil. Trans.*, **225**, 357 (1926).

of character in definition. Then, again, the constant separation of the lines arising from the same pair of levels was of less value than in ordinary spectra, since the first members only of any series could be identified with certainty, the remainder being either too faint or else inextricably mixed up with the enormous number of lines present in these spectra. For this reason it was not possible to use a series formula to calculate the limits or terms and to check the results. These difficulties seem to be formidable enough, but they were overcome in a very striking fashion. The results and the details of the work cannot be given here, it being sufficient to say that the latter were based on an elaboration of the methods we have already discussed.

CHAPTER II.

THE ZEEMAN EFFECT.

Introduction and Early Work.—In 1896 Zeeman discovered that if a Bunsen flame fed with small quantities of sodium were placed between the poles of a powerful electro-magnet, and its spectrum examined, then, when the exciting current was turned on, the D lines were seen to be broadened, regaining their original appearance when the exciting current was cut off. This was also found to be the case when the reversed D lines, obtained in the usual way by absorption, were examined in the same way. Zeeman pointed out that the phenomenon is a natural consequence of H. A. Lorentz's theory of electromagnetic radiation. When a substance is placed in a magnetic field, the motion of the electrons are influenced so that changes are made in their periods of vibration. Zeeman showed that, as a simple result of this theory, the motions of the electrons may be resolved into three components, one in straight lines parallel to the magnetic lines of force, and the other two at right angles to them; the two last may be resolved into two circular motions (right- and left-handed) round an axis parallel to the lines of force. Evidently the first rectilinear motion will not be influenced by the magnetic field, whilst, on the other hand, the two circular motions will be altered, the vibration period of one being accelerated and that of the other being decelerated. If the lines of force of the magnetic field are parallel to the line of vision, then, the electrons being negatively charged, the right-handed motion will be retarded and the left-handed motion accelerated. On these grounds it is easy to predict the effect on the lines of a spectrum.

Let us consider, in the first place, the effect if we examine the light evolved from some source placed in a powerful magnetic field, looking along the lines of force. Under these circumstances the first component of the motion of the electrons, that is to say, those electrons moving parallel to the lines of force, cannot emit any light in our direction, since they are not moving transversely to the line of vision; these particles are simply moving backwards and forwards in the sight line, and therefore they will give rise to light waves at right angles to the sight line, but not in directions parallel to it. The two circular components, on the other hand, will give rise to two circularly polarised rays, and as the one circular component is accelerated,

and the other retarded by the magnetic field, the two resulting circularly polarised rays will have different oscillation frequencies; with a sufficiently powerful spectroscope these two rays will be seen separated. Since the action of the magnetic field restrains one of the circular motions just as much as it accelerates the other, it follows that we should see in the spectroscope, instead of a single line, a doublet, whose components are situated at an equal distance on either side of the position of the original line, and are circularly polarised, one in the right-handed, and the other in the left-handed, sense.

If now, in the second place, the light be viewed across the lines of force, then effects will be produced by all three components. The first component, that is the electrons vibrating parallel to the magnetic lines of force, will give rise to waves which are plane polarised, the vibrations being parallel to the lines of force. Since these motions are not influenced by the magnetic field, the oscillation frequency of the resulting waves will be the same as that of the undisturbed light. The two circular components will now be seen sideways, and the electrons will act as if they were simply vibrating in straight lines up and down, or perpendicular to the lines of force. They will thus give rise to plane polarised light waves, the vibrations being perpendicular to the lines of force. As in the previous case, since the two circular motions have not the same period, therefore two of these plane polarised rays will be emitted, one having an oscillation frequency greater and the other less than that of the original light. When, therefore, the light is viewed across the lines of force, each spectrum line should be seen to be split symmetrically into three lines, and each line should be plane polarised, the two outside components having their plane of polarisation parallel to the lines of force, and the middle component with its plane of polarisation perpendicular to the lines of force.

With the apparatus at his disposal, Zeeman [1] was not at first able to split the spectrum lines into doublets or triplets, but he found that the lines were widened, and that the edges were polarised exactly in the way he expected from the theory. In order to view the light along the lines of force, he took an electro-magnet with holes bored through the poles, and so placed it that the axes of the holes and the centre of the diffraction grating were on the same straight line. Between the grating and the eyepiece were placed a quarter-wave plate, to convert the circular polarised light into plane polarised, and a Nicol prism. The plate and the Nicol were relatively placed in such a way as to extinguish right-handed circularly polarised light, and the cross-wires of the eyepiece were set upon the bright line as seen. When the current through the magnet was reversed, the spectrum line was seen to move. Without the use of the quarter-wave plate and the Nicol a widened line was seen. The quarter-wave plate and the Nicol extinguished the one edge which was circularly polarised in the right-handed direction; on reversing the current the other edge now

[1] *Phil. Mag.* (5), **43**, 226 (1897).

became circularly polarised in the right-handed sense, and was extinguished, so that the line appeared to move its position. Similarly Zeeman was able to prove that when the light was examined across the lines of force, the widened line then seen had its edges plane polarised, the plane of polarisation being perpendicular to the length of the line. Michelson [1] was able, by means of his interferometer, to show that the components of a line could be separated, and afterwards Zeeman [2] succeeded in seeing with a grating spectroscope both the magnetic doublet and triplet with the cadmium line $\lambda = 4800$.

In a later paper, Zeeman [3] published some results of measurements between the two outer components of some triplets obtained by viewing the light across the lines of force. The sharp spectra of zinc, cadmium, copper, and tin were used, condensed sparks from an induction coil being made to pass between electrodes of the particular metal, and the poles of the magnet were brought up as close to the spark as possible without disturbing it. The resulting triplets were photographed, the middle component being extinguished by means of a Nicol prism, so as to leave the two outer components free from any contamination, and thus more readily measurable. Zeeman found that the separation of the two outer components varied considerably from line to line even in the same spectrum; for example, in the case of the three zinc lines $\lambda = 4811$, $\lambda = 4722$, and $\lambda = 4680$, the separation was equal to 0·8, 0·9, and 1·1 A.U. respectively, while with the three lines $\lambda = 3345$, $\lambda = 3303$, and $\lambda = 3282$ the separation was too small to be measured. It is important to notice, as Zeeman pointed out, that the first-mentioned lines belong to the sharp series, while the last three belong to the diffuse series. Exactly similar results were obtained with the other metals named. This was the first evidence that lines of different spectral series behave differently in the negative field.

Preston,[4] who worked with a full-size Rowland grating, found that the "normal triplet" is by no means always obtained when a line is examined across the lines of force, but that doublets, quartets, and sextets are often obtained. Analysis of these groups by a Nicol prism showed, however, that they could all be considered as derived from the normal triplet, the doublet by the absorption of the middle line, the quartets either by the doubling of the middle line or the absorption of the middle line and doubling of the two outer components, and the sextet by the doubling of all three lines of the triplet. As the result of his observations on magnesium, zinc, and cadmium, Preston was able to prove that the Zeeman phenomenon, or as we may call it, the Zeeman pattern, is the same for all the lines of any one spectral series, the pattern in each case being characteristic of the series. He further proved that the Zeeman patterns given by lines of the same series type, but belonging to different elements, are

[1] *Phil. Mag.*, **44**, 109 (1897).
[2] *Ibid.*, **44**, 55 and 255 (1897).
[3] *Ibid.* (5), **45**, 197 (1898).
[4] *Ibid.* (5), **45**, 325 (1898).

the same. Expressing this in modern language, the Zeeman pattern is dependent only on the spectral combination (sp_i) $(p_id_i$, etc.), and is independent of the order number of the line and of the atomic number of the element. This was proved, both qualitatively and quantitatively, and is known as Preston's law.

As has already been stated, the Zeeman triplet is a natural consequence of the Lorentz electro-magnetic theory, and it can be shown that the separation of the triplet can be calculated from this theory. Preston was the first to prove quantitatively that the separation is directly proportional to the strength of the magnetic field, and from the Lorentz theory it can be proved that the separation of the two outer components is given in electro-magnetic units by

$$\Delta\nu = \frac{e}{m} \cdot \frac{\mathrm{H}}{4\pi v} = 4{\cdot}70 \times 10^{-5} \times \mathrm{H}$$

where $\Delta\nu$ is expressed in wave-numbers, e/m is the ratio of charge on the electron to its mass, H is the strength of the field expressed in Gauss, and v is the velocity of light. The separation value $4{\cdot}70 \times 10^{-5} \times \mathrm{H}$ is known as that of the normal triplet or Lorentz triplet.

As the investigations of the Zeeman phenomenon were extended by various observers, it was soon found that the normal triplet is by no means a common phenomenon and that only a few lines exhibit this simple structure. It is true that many lines exhibit triplets, but the separations of these triplets are not the same as that of the normal or Lorentz triplet. In view of the fact that the theory led to the normal triplet, all other Zeeman patterns were given the name of anomalous Zeeman effects, and this name has continued to be used up to the present day, in spite of the fact that the modern theory has explained them as well as the normal triplet.

In this introductory account of the early work on the Zeeman effect there is no need to give a full description of the experimental results which were obtained. The enunciation of the Bohr theory of spectral series threw an entirely new light on the phenomenon and it was not until the energy quantum theory was applied to the Zeeman effect by Sommerfeld and by Landé that any real understanding of the anomalous Zeeman pattern was obtained. All the experimental observations in these early days which we at present have under review were undertaken as it were in the dark, and many *ad hoc* explanations were brought forward, only to be abandoned at a later date. It is quite impossible, and certainly unnecessary, to enter into any detail of the greater part of this work. I propose therefore now only to describe as much of this early work as laid the foundations on which the present-day theory has been based. In the next section the theory of the Zeeman effect will be discussed and its application to experimental observations. Lastly, we may deal with the experimental technique, including the apparatus and methods of measurement.

Keeping within the limitations set for this introductory section,

the most important work to which reference must be made was carried out by Runge and Paschen[1] in the direction of observation and measurement of many anomalous Zeeman patterns. First may be considered the resolution of the lines of the sharp triplet series of mercury. The three lines of each triplet give three different Zeeman patterns, one for each line. These three patterns are the same whatever is the order number of the triplet and the measurements of each characteristic pattern, when expressed in wave-numbers, are the same in a constant field and are directly proportional to the field. This is in accord with Preston's law.

The measurements given by Runge and Paschen in wave-numbers for a field of about 23,000 Gauss were as follows, the letters p and s denoting polarisation parallel to and at right angles to the lines of force, respectively.

Combination.	s.	s.	s.	p.	p.	p.	s.	s.	s.
(sp_1)	− 2·13	− 1·62	− 1·07	− 0·53	0	+ 0·55	+ 1·06	+ 1·63	+ 2·17
(sp_2)	− 2·15	− 1·62		− 0·57		+ 0·54		+ 1·64	+ 2·16
(sp_3)	− 2·17				0				+ 2·17

A diagram of the three anomalous patterns is shown in Fig. 29.

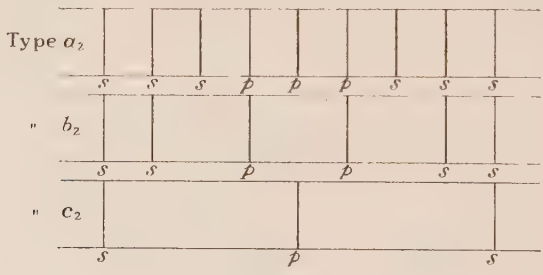


FIG. 29.

The triplet shown by the third line (sp_3) is not a normal triplet, since the separation is twice that of the normal triplet. As another instance we may take the anomalous Zeeman patterns of the principal pairs in the doublet system, such, for example, as the D lines of sodium. Runge and Paschen's measurements with a field of about 30,000 Gauss were

	s.	s.	s.	p.	p.	p.	p.	s.	s.	s.
D_2	− 2·28		− 1·43		− 0·47	+ 0·46		+ 1·35		+ 2·36
D_1		− 1·88		− 0·90			+ 0·93		+ 1·85	

a diagrammatic representation being given in Fig. 30.

[1] *Astrophys. Journ.*, **15**, 157, 333 (1902); *Phys. Zeitsch.*, **3**, 443 (1902); *Berl. Ber.*, 380, 720 (1902).

The principal series of doublets of copper and silver also show exactly the same types with identical separations in the same field. The sharp series of doublets of these elements show the same types but in the reversed sense, that is to say, the line with the smaller wave-number shows the D_2 pattern, whilst the line with the larger wave-number shows the D_1 pattern. This phenomenon is of course fully in keeping with spectral series phenomena, and it indicates, though this was not recognised, that the Zeeman pattern depends in some way on the combination of terms to which the line is due.

If the measurements given above for a sharp triplet and a principal doublet be examined it will be seen that a very simple relation exists for each. For example, the measurements of the latter can be expressed as

$$\left.\begin{array}{llll} D_2 & \pm x & \pm 3x & \pm 5x \\ D_1 & \pm 2x & \pm 4x & \end{array}\right\} \text{where } x = 0{\cdot}463.$$

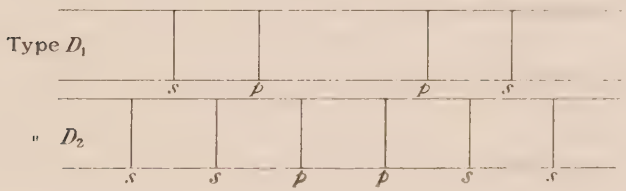


FIG. 30.

Again, the anomalous Zeeman patterns of the sharp triplet can be expressed as

$$\left.\begin{array}{llll} (sp_1)\ 0 & \pm y & \pm 2y & \pm 3y \quad \pm 4y \\ (sp_2) & \pm y & & \pm 3y \quad \pm 4y \\ (sp_3)\ 0 & & & \pm 4y \end{array}\right\} \text{where } y = 0{\cdot}54.$$

Now in the case of the D lines the field strength was about 30,000 Gauss, and therefore the normal triplet separation is $\pm 4{\cdot}70 \times 10^{-5} \times 30{,}000$ or $1{\cdot}41$ cm.$^{-1}$. It follows that x is one-third of the normal triplet interval and that the anomalous pattern of the D lines can be expressed as

$$\left.\begin{array}{llll} D_2 & \pm \frac{1}{3}a & \pm \frac{3}{3}a & \pm \frac{5}{3}a \\ D_1 & \pm \frac{2}{3}a & \pm \frac{4}{3}a & \end{array}\right\} \text{where } a \text{ is the normal triplet interval or } \Delta\nu_{\text{norm}}.$$

Again, in the case of the sharp triplet the field strength was 23,000 Gauss, and therefore the normal triplet interval is $\pm 4{\cdot}7 \times 23{,}000$ or $\pm 1{\cdot}08$ cm.$^{-1}$. It follows that y is one-half the normal triplet interval and the anomalous patterns of the sharp triplet can be expressed as

$$\begin{array}{llllll} (sp_1)\ 0 & \pm \frac{1}{2}a & \pm \frac{2}{2}a & \pm \frac{3}{2}a & \pm \frac{4}{2}a \\ (sp_2) & \pm \frac{1}{2}a & \pm \frac{3}{2}a & \pm \frac{4}{2}a & \\ (sp_3)\ 0 & \pm \frac{4}{2}a & & & \end{array}$$

This relationship was discovered by Runge,[1] and he showed that all the anomalous Zeeman patterns known at that time can be expressed as rational multiples of $\Delta\nu_{\text{norm}}$, that is to say, as integral multiples of a/r, where r is an integral number called the Runge denominator. This is known as Runge's law and has proved of fundamental significance in arriving at the true explanation of the anomalous Zeeman effect. In the two instances quoted above the values of the Runge denominator were 3 and 2, these being characteristic of the principal and sharp series of doublets and the principal and sharp series of triplets, respectively. The values of r are larger in the case of other series, for example $r = 15$ in the diffuse series of doublets and $r = 6$ in the diffuse triplet series.

There is one further phenomenon to which reference must be made at this stage in order to serve as an introduction to its subsequent discussion and explanation. This phenomenon is the asymmetry of the anomalous Zeeman pattern and its distortion. This was first observed by Zeeman [2] with the yellow mercury line at $\lambda = 5791$ which gives an asymmetric triplet in which the separation of the blue component is less than that of the red component with respect to the central line. The difference between the two separations in fields of 15,000-30,000 Gauss amounted to from 0·025 to 0·048 A. This was criticised by Gmelin [3] and by von Baeyer and Gehrcke,[4] but definitely established by Zeeman [5] with the use of a Fabry and Perot étalon. Dufour also showed that Zeeman patterns given by certain lines of chromium exhibit asymmetry, the asymmetry being proportional to the square of the field strength. As the experimental technique has improved the presence of asymmetry in greater or less degree has become more and more frequently recognised, and indeed it may be said that it is generally present. The accurate expression of an anomalous Zeeman pattern by rational multiples of the normal triplet interval is an ideal to which the actual measurements only approximate, but, as will be shown later, the distortion is generally of a type which can be corrected in a very simple manner.

With the foregoing facts at our disposal we may now turn to the theory of the Zeeman effect.

The Theory of the Zeeman Effect.—During the last few years the energy quantum theory has been applied to the Zeeman effect with the most interesting and important results. The first to succeed in doing this was Sommerfeld who first of all gave the explanation of the normal triplet and then, by enunciation of his law of magneto-optic resolution, paved the way to the explanation of the theory of the anomalous Zeeman effect as observed with doublet and triplet systems. This explanation was found by Landé. Subsequently Sommerfeld was

[1] *Phys. Zeitsch.*, **8**, 232 (1907).
[2] *Konink. Akad. Wetensch. Amsterdam, Proc.*, **10**, 551 (1907).
[3] *Phys. Zeitsch.*, **9**, 212 (1908).
[4] *Deutsch. Phys. Ges. Verh.*, **10**, 357, 423 (1908).
[5] *Konink. Akad. Wetensch. Amsterdam, Proc.*, **11**, 440 (1908).

successful in applying the quantum theory to the Paschen-Back effect,[1] and then Landé by a very remarkable advance was able to formulate a general theory which has enabled him to find the theoretical explanation of the complete Zeeman phenomenon as evidenced by systems of all multiplicities, not only of the first but also of the second order of complexity as instanced by the case of neon.

In discussing these advances it is necessary for us to deal with them step by step as they were made in order to gain an understanding of them. It must be remembered that these later developments of the theory of the Zeeman effect have led to most important extensions of our knowledge of the more complex systems involved in spectral series, which in their turn have materially assisted progress in the complete elucidation of the magnetic resolution of series lines. The progress has thus been such that it is difficult to discuss the two fields of work separately. The importance of the newer developments of the theory of the Zeeman effect in relation to the newer advances in our knowledge of spectral series has already been implied if not definitely expressed in Chapter I. The intimate relation between the two fields will perhaps be more apparent from what follows.

The remarkable work of Landé on the theoretical side owes not a little to the brilliant work of Back on the experimental side. To him, in conjunction with Paschen, we owe the discovery of the Paschen-Back effect, and, further, by his individual observations the Landé theory has found a complete experimental verification.

In Chapter I. on series of lines in emission spectra we dealt with Sommerfeld's work on the quantising of the Kepler orbits with respect to size and form by means of the azimuthal quantum number k and the radial quantum number r. It is now necessary to extend this to the quantising of the electron orbits in space and show that in this way the position of the orbits can be determined, that is to say, the quantum theory selects from all possible positions of the orbits a discrete number which conform to certain quantum conditions. It is of course only possible to carry out this spatial quantisation when a certain favoured direction is given with respect to which the orientation of the orbits may be measured. This may be given either by an external field of force or by an internal atomic field, and the former will be considered here.[2] Even in this case for the hydrogen atom we have not true Kepler orbits, since these are deformed through the external field of force. If, in spite of this, we wish to deal with the Kepler orbit we must pass to the limit when the external field tends to zero. In this passage to the limit the disturbance of the orbits by the field of force vanishes, whilst the possibility of their orientation with respect to the field of force remains. The reason for this is that, whereas the disturbance of the orbits varies continuously with the field of force,

[1] See below, p. 371.

[2] *Ann. der Phys.*, **51**, 1 (1916); *Phys. Zeitsch.*, **17**, 491 (1916); see also *Atombau und Spektrallinien*, 4th Auflage, pp. 130 and 386, Vieweg, Braunschweig, 1924.

the orientation of the orbits is restricted to certain discrete possibilities. That is why the latter remains after the passage to the limit, whereas the former vanishes.

In place of the two degrees of freedom dealt with in Chapter I. we have now three degrees of freedom, q, θ, ψ, and corresponding to these there are three quantum conditions

$$\int p_q dq = rh, \qquad \int p_\psi d\psi = n_1 h, \qquad \int p_\theta d\theta = n_2 h \qquad . \quad (1)$$

The first or radial quantum integral does not differ from that in the two dimensional problem, and as was shown on p. 105 it gives

$$2\pi p\left(\frac{1}{\sqrt{1-\epsilon^2}} - 1\right) = rh \qquad . \quad . \quad . \quad (2)$$

and determines the form of the orbit through the eccentricity ϵ. p is the areal constant for the orbital azimuth ϕ and as before

$$\int_0^{2\pi} p d\phi = 2\pi p = kh \qquad . \quad . \quad . \quad . \quad (3)$$

where k is the azimuthal quantum number. The quantum numbers n_1 and n_2 are known as the equatorial and latitudinal quantum numbers respectively, and it may be shown that the azimuthal quantum number is equal to the sum of the equatorial and latitudinal quantum numbers, that is to say

$$k = n_1 + n_2 \qquad . \quad . \quad . \quad . \quad (4)$$

It can also be shown that

$$n_1 = k \cos \alpha \qquad . \quad . \quad . \quad . \quad (5)$$

where α is the angle between the direction of the lines of force and the normals to the orbital plane. Combined with (4) equation (5) states that

$$\cos \alpha = \frac{n_1}{n_1 + n_2} \qquad . \quad . \quad . \quad . \quad (6)$$

and that there are certain quantum favoured spatial positions of the orbital plane characterised by integral numbers. This conclusion, in Professor Sommerfeld's own words, is without doubt one of the most surprising results of the quantum theory.

It must be remembered that, so long as we deal with the limiting case of the external force tending to zero, the present results have no effect on the calculation of the energy of the orbits and hence no bearing on the ordinary phenomenon of spectral series. The equatorial and latitudinal quantum numbers then enter into the expression for the energy only in the form of their sum, namely, the azimuthal quantum number. In other words, the expression for the energy and the frequencies of the spectrum lines derived therefrom remain the same as in the simple case of the plane quantisation. On the other hand, in the case of a true field of force the existence

of three quantum conditions becomes essential. Under these conditions it may be shown that in the meridian position of the orbital plane the electron, under the influence of an electric force acting in this plane, would finally collide with the nucleus. This may also be taken for granted in the limiting case when the external force tends to zero, and consequently the number of spatial possibilities must be reduced by one, namely, the meridian position characterised by $n_1 = 0$, $\cos \alpha = 0$. Sommerfeld states his final conclusion in the following words: For any arbitrary azimuthal quantum number k there are exactly k quantised positions of the orbital plane which are characterised by whole numbers. They correspond to all resolutions of the number k into $n_1 + n_2$, including $n_2 = 0$ (the equatorial position of the orbital plane), and excluding $n_1 = 0$ (the meridian position). These k positions are constructed by dividing a radius of the equator of the unit sphere into k equal parts and erecting on the dividing points (excluding the centre of the unit sphere) right-angled triangles. These figures themselves are to be corrected by removing the diameter which is at right angles to the equatorial plane from the series of the projections of the orbital planes.

We may now apply the above deductions to the Zeeman phenomenon and show in the first place how the normal Zeeman effect can be understood on the quantum theory, making use of the simplest atom, namely, that of hydrogen. In the preceding, the orbits of the electron have been spatially quantised for a field of force of zero intensity and the action of an arbitrary homogeneous magnetic field can be reduced to this case, since the superimposed field leaves the form of the orbits and their inclination to the magnetic lines of force, together with the motion of the electron in the orbit, unchanged, and leads only to the addition of a uniform precession of the orbit about the direction of the lines of force.[1] The precessional velocity is given by

$$\mathbf{o} = \frac{e\mathrm{H}}{2mv} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where the symbols have the same meaning as on p. 311. This law holds, provided that the velocity imparted to the electron by the precessional motion is small compared with its normal velocity, and indeed this is the case for the hydrogen atom under the strongest magnetic field that can be produced.

Sommerfeld next proves that in the magnetic field the electron describes the same path as in the absence of the field, but does so with respect to a system of reference which is rotated with a velocity $\mathbf{o}$ determined by (7). The precession of the system of reference and the action of the magnetic field are therefore equivalent to one another and interchangeable. It follows that, if we carry over the quantising of the fieldless orbits from the static system dealt with

[1] Larmor's Theorem.

above to the precessional system of reference, we shall obtain for the quantised orbits with a field the same orbits in the precessional system of reference as we obtained for the static system without a field. The quantum conditions therefore are set up for the magnetic field as in the limiting case when the field was zero.

By introducing the polar co-ordinates q, ϕ, ψ, in the precessional system of reference we have

$$\int p_q dq = rh, \qquad \int p_\psi d\psi = n_1 h, \qquad \int p_\theta d\theta = n_2 h \quad . \quad (8)$$

from which, as previously,

$$\left.\begin{aligned} &2\pi p\left(\frac{1}{\sqrt{1-\epsilon^2}} - 1\right) = rh, \quad \cos\alpha = \frac{n_1}{n_1 + n_2}, \quad 2\pi p = (n_1 + n_2)h \\ &\text{and also} \qquad\qquad p_\psi = \frac{n_1 h}{2\pi} \end{aligned}\right\} \quad (9)$$

The quantities ϵ and θ are independent of whether they are referred to the static or precessional system of reference, whilst the quantities p and p_ψ are to be measured in the system of reference which is turned with velocity $\mathbf{o}$.

Sommerfeld then calculates the kinetic energy of the electron in the magnetic field, E(H), and the kinetic energy in the absence of the field, E(O), and he shows that

$$\mathrm{E(H)} = \mathrm{E(O)} + p_\psi \mathbf{o} \quad . \quad . \quad . \quad (10)$$

The change in the kinetic energy caused by the magnetic field H is given by

$$\Delta\mathrm{E} = \mathrm{E(H)} - \mathrm{E(O)},$$

whence, by substituting the value of p_ψ given in (9),

$$\Delta\mathrm{E} = \frac{n_1 \mathbf{o} h}{2\pi} \quad . \quad . \quad . \quad . \quad (11)$$

The potential energy of the Coulomb attraction, $-\frac{e^2}{r}$, is not changed, since the distance r in the precessional and original orbits is the same within the present limits of accuracy, and hence

$$\Delta\mathrm{E}_{\mathrm{pot}} = 0.$$

The magnetic change in the total energy, W, of the electron is therefore

$$\Delta\mathrm{W} = \frac{n_1 \mathbf{o} h}{2\pi} \quad . \quad . \quad . \quad . \quad (12)$$

and the difference of the total energy in the initial and final orbit of the electron is given by

$$\Delta\mathrm{W}_a - \Delta\mathrm{W}_e = \frac{n_{1_a} - n_{1_b}}{2\pi} \mathbf{o} h \quad . \quad . \quad . \quad (13)$$

As was shown in Chapter I. the frequency of a spectrum line according to Bohr's condition is given by

$$h\nu = E_1 - E_2,$$

where E_1 and E_2 are the energies of the final and initial orbits of the electron. The effect of the magnetic field is therefore given by

$$h\Delta\nu = \Delta W_a - \Delta W_b = \frac{n_{1_a} - n_{1_b}}{2\pi} \mathbf{o} h,$$

and if we substitute the value for **o** given in equation (7) we have

$$\Delta\nu = (n_{1_a} - n_{1_b}) \frac{eH}{m4\pi v}. \quad . \quad . \quad . \quad (14)$$

Just as in Bohr's theory of spectral series, the quantum of action, h, has cancelled out and consequently in (14) the quantum theory has, in a sense, become latent. It may be noted that in this may be found a reason why Lorentz was able to develop his theory on classical electro-magnetic lines.

In order to complete the development of formula (14) it is only necessary to apply the principle of selection which in the case of the magnetic field only concerns the equatorial quantum number n_1.

This principle was first enunciated by Rubinowicz [1] and its application in the phenomena of spectral series was dealt with in Chapter I. We are now concerned with the equatorial quantum number n_1 and the selection principle states that changes in this number are restricted to unity or zero, that is to say

$$(n_{1_a} - n_{1_b}) = \pm 1 \text{ or } 0. \quad . \quad . \quad . \quad (15)$$

We have therefore

$$\Delta\nu = \pm \frac{eH}{m4\pi v} \text{ or } \Delta\nu = 0. \quad . \quad . \quad . \quad (16)$$

This result is identical with that deduced from the Lorentz theory, for equation (16) not only gives the two lines of the Zeeman triplet, which are displaced by the amount $\Delta\nu$ towards the greater and smaller frequencies respectively, but also the undisplaced component.

The polarisation of the three components is also explained because Rubinowicz showed that in a field of force the vibrations due to the quantum jump $\Delta n_1 = \pm 1$ are circularly polarised with respect to the lines of force, whilst the vibrations due to the quantum jump $\Delta n_1 = 0$ are linearly polarised in a direction parallel to the lines of force. It therefore follows from (16) that when viewed along the lines of force the two external components only are visible and that these are circularly polarised in opposite directions. When viewed transversely to the lines of force the two external components are

[1] *Phys. Zeitsch.*, **19**, 441, 465 (1918).

linearly polarised at right angles to the lines of force ; in this case the central undisplaced component is visible and is linearly polarised parallel to the lines of force.

We may now consider the various quantum number transitions which are possible and take as our instance the red line of hydrogen H_α. As was shown in Chapter I. the wave-number of this line is given by

$$\nu = N\left(\frac{1}{2^2} - \frac{1}{3^2}\right) \quad . \quad . \quad . \quad . \quad (17)$$

The total quantum number of the initial orbit is therefore 3 and that of the final orbit 2. The total quantum number is the sum of the radial, latitudinal, and equatorial quantum numbers, and we thus have $r + n_2 + n_1 = 3$ for the initial orbit, and for the final orbit we may write $R + N_2 + N_1 = 2$. It follows from what was said above that in the transition $N_1 = n_1$, parallel polarised components will be obtained, and perpendicularly polarised components in the transitions $N_1 = n_1 \pm 1$.

We are now in a position to enumerate the quantum number transition for the *p*- and *s*- components of the H_α line, and these are given in Tables CXLVII. and CXLVIII., it being remembered that the selection principle does not apply to the radial quantum number and that, as previously stated, the value $n_1 = 0$ is excluded. Table CXLVII. contains all the possible transitions $RN_2N_1 \rightarrow rn_2n_1$ for which $N_1 = n_1$ and $R + N_2 + N_1 = 3 \rightarrow r + n_2 + n_1 = 2$; similarly Table CXLVIII. contains all the possible transitions for which $N_1 = n_1 \pm 1$.

TABLE CXLVII.

H_α *p*-components, $\Delta n_1 = 0$.

$RN_2N_1 \rightarrow rn_2n_1$
012 → 002
(102 → 002)
111 → 101
(111 → 011)
(201 → 101)
201 → 011
021 → 011
(021 → 101)

TABLE CXLVIII.

H_α *s*-components, $\Delta n_1 = \pm 1$.

$RN_2N_1 \rightarrow rn_2n_1$
003 → 002
102 → 101
(102 → 011)
012 → 011
(012 → 101)
201 → 002
021 → 002
(111 → 002)

In Chapter I. it was stated that the selection principle restricts the transitions in the azimuthal quantum number k to $\Delta k = \pm 1$. Since $k = n_2 + n_1$, it follows that all transitions are forbidden except those in which $N_2 + N_1 = n_2 + n_1 \pm 1$. The forbidden transitions are bracketed in the above tables.

It must of course be noted that all the remaining transitions given in Table CXLVII. conform to the condition $\Delta n_1 = 0$ and that from the present standpoint they all lead to the central component of the normal triplet. In the second table the same is true, but here the transitions give two components displaced in opposite directions by

the normal triplet interval. As has already been shown in Chapter I. the individual transitions become of importance when the phenomenon is treated from the standpoint of relativity.

The Anomalous Zeeman Effect.– We may next turn our attention to the application of the quantum theory to the anomalous Zeeman effect, and once again are we indebted to Sommerfeld in that it is largely due to him that the problem has been solved and a complete explanation found of this phenomenon. The first step made by him was the enunciation of his law of magneto-optic resolution which deals with the Runge denominator.[1] Just as in the general theory of spectral series the combination principle is the fundamental basis, so Sommerfeld starts from the point of view that the same principle must also hold for the anomalous Zeeman effects. The magneto-optical resolution denotes the transition of the atom from an initial to a final configuration. The magnetic field influences the energy of the initial and final configurations separately, and also influences separately the two terms the difference in which denotes the spectral series line. If the frequency of the line is denoted by $\nu = \nu_1 - \nu_2$ then the magnetic resolution of the line is given by

$$\Delta\nu = \Delta\nu_1 - \Delta\nu_2. \quad . \quad . \quad . \quad . \quad (18)$$

By Runge's rule we have

$$\Delta\nu = \frac{q}{r}\Delta\nu_{\text{norm}}, \quad . \quad . \quad . \quad . \quad (19)$$

but the basis of this formula is to be found in the behaviour of the two terms, and consequently we may write

$$\Delta\nu_1 = \frac{q_1}{r_1}\Delta\nu_{\text{norm}} \quad \text{and} \quad \Delta\nu_2 = \frac{q_2}{r_2}\Delta\nu_{\text{norm}}. \quad . \quad . \quad (20)$$

It follows from (18) and (19) that

$$\frac{q}{r} = \frac{q_1}{r_1} - \frac{q_2}{r_2} = \frac{q_1 r_2 - q_2 r_1}{r_1 r_2}. \quad . \quad . \quad . \quad (21)$$

Since $\frac{q}{r}$, $\frac{q_1}{r_1}$, and $\frac{q_2}{r_2}$ are all rational numbers, it follows that the intervals between the components of the magnetically resolved line are integral multiples of the product $r_1 r_2$. We arrive at the conclusion, therefore, that

$$r = r_1 r_2 \quad . \quad . \quad . \quad . \quad . \quad (22)$$

or, in words, that the Runge denominator of a given spectrum line resolves into the Runge denominators of the two spectral terms of that line and is composed of their least common multiple. This is Sommerfeld's law of magneto-optic resolution. This law is of considerable importance since it not only enables us to resolve the observed Runge denominators into smaller factors, but it endows them with a meaning that is accessible to observation.

[1] *Ann. der Phys.*, **63**, 221 (1920); *Atombau und Spektrallinien*, p. 612.

In applying this law to experimental facts we may first take the case of simple lines which exhibit the normal Zeeman effect. It is obvious that in these lines

$$r = 1,$$

and that for the two spectral terms which compose such lines

$$r_1 = r_2 = 1.$$

Since the sharp term of any series system whatsoever is a simple term, even in the case of complex systems, we may state as our starting point that the Runge denominator of the sharp term in any combination is always equal to 1.

In the case of doublet systems, the principal and sharp series exhibit, as described on p. 313, a magnetic resolution for which the Runge denominator $r = 3$. Since in both series the value of r_1 for the sharp term is 1, it is obvious that the value of r_2 for the π term must be 3. In the diffuse ($\pi\delta$) series where the Runge denominator is 15, there are two possibilities. We have already found that r_1 for the π term is 3 and since the value of $r = 15$ is the least common multiple of r_1 and r_2, the value of r_2 for the δ term may be either 5 or 3×5. On the simpler assumption that $r_2 = 5$ we have the following scheme for the Runge denominators of the various terms of the complete doublet system:—

σ	π	δ	ϕ	x	y
1	3	5	7	(9)	(11)

the numbers in brackets being extrapolated.

In the case of the triplet systems the Runge denominator of the principal and sharp series is 2 and consequently, since again we have $r_1 = 1$ for the sharp term, $r_2 = 2$ for the principal term. In the diffuse (pd) series the Runge denominator is 6 and therefore the value of r_2 may either be 3 or 2×3. It is possible here to choose between these two alternatives by reference to the combination (Pd) between the singlets and diffuse terms. Since in the case of all singlets $r = 1$, it follows that the Runge denominator of the lines of this combination must be identical with that of the diffuse term. The observed Runge denominator of the Pd combination is 6 and therefore the value of r_2 for the d term must be 2×3. Sommerfeld gives the following scheme for the values of the Runge denominators of the various terms in the triplet series:—

s	p	d	f	x	y
1	1×2	2×3	3×4	(4×5)	(5×6)

the two last values again being extrapolated.

It is obvious that the magneto-optic resolution law of Sommerfeld has done much to simplify the apparently complex nature of the anomalous Zeeman effect as is shown in weak magnetic fields. The knowledge of the Runge denominators which we have gained gives

us the first step towards the formulation of the complete theory of the Zeeman effect.

For the solution of the problem of the anomalous Zeeman effect we are indebted to Landé who applied Sommerfeld's law of magneto-optic resolution and also his conception of inner quantum numbers, together with the selection principle and the rule of polarisation. There is no need to give a detailed account of the various stages in the development of Landé's theory owing to the fact that the later advances in our knowledge of the multiple terms, dealt with in Chapter I., enabled him to make a remarkable generalisation which renders unnecessary any reference to some of the earlier intermediate steps. In order to understand the later work it is, however, incumbent on us to consider in some detail his first step, namely, the explanation of the anomalous Zeeman effect as observed with the spectrum lines of elements having doublet systems, such for example as sodium,[1] even though here we must make use of the values for the various quantum numbers as fixed by the later work.

As may be seen from the account given above of Sommerfeld's application of the quantum theory to the normal Zeeman effect, the original energy of the Kepler orbits W_0 becomes changed by the magnetic field into

$$W = W_0 + mho, \quad . \quad . \quad . \quad . \quad (23)$$

if we replace the equatorial quantum number n_1 by m and write o for the normal triplet interval.

In the case of doublet systems Landé put forward the equation

$$W = W_0(I) + mh\frac{2I}{r}o \quad . \quad . \quad . \quad . \quad (24)$$

The original energy is different for the two doublet levels and this is the meaning of the symbol $W_0(I)$. In the second term on the right-hand side I is the Landé value of Sommerfeld's inner quantum number [2] and r is the Runge denominator for the particular term level. In the following account of Landé's work it is necessary throughout to adopt his values of I in preference to the i of Sommerfeld.

In this expression m has the values

$$m = \pm\tfrac{1}{2}, \quad \pm\tfrac{3}{2}, \quad \pm\tfrac{5}{2}, \ldots \pm(I - \tfrac{1}{2}) \quad . \quad . \quad (25)$$

It follows that the application of a magnetic field resolves each individual term level into a definite number of magnetic levels, the number of which is equal to $2I$, the maximum value of m being $\pm(I - \frac{1}{2})$.

It is obvious from (24) that the energy difference between the original undisturbed level and the first magnetic level will be given by I/r, whilst the energy difference between any two consecutive magnetic levels will be given by $2I/r$ since the difference between any two consecutive values of m is unity. We may now set out the values

[1] *Zeitsch. für Phys.*, **5**, 231 (1921). [2] See p. 146.

of I and r for each of the term levels of a doublet system, the values of I having already been given on p. 148 and the values of r being those of Sommerfeld as explained above.[1]

	I	r
σ	1	1
π_2	2	3
π_1	1	3
δ_3	3	5
δ_2	2	5
ϕ_4	4	7
ϕ_3	3	7

We have, therefore, for the difference between two successive magnetic levels

σ	π_2	π_1	δ_3	δ_2	ϕ_4	ϕ_3
2	$\frac{4}{3}$	$\frac{2}{3}$	$\frac{6}{5}$	$\frac{4}{5}$	$\frac{8}{7}$	$\frac{6}{7}$

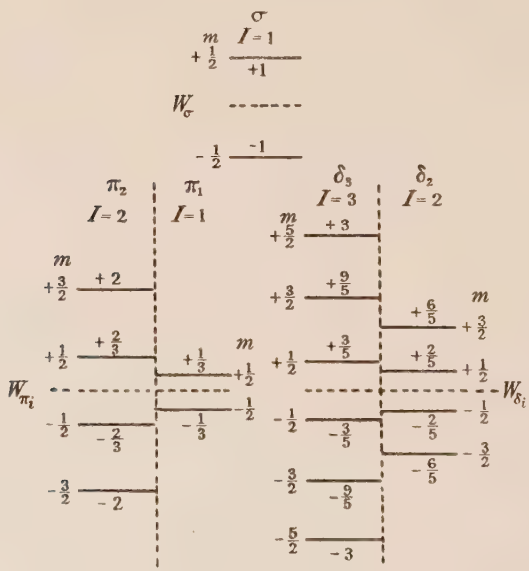


FIG. 31.

all these values, of course, being in terms of $\Delta\nu_{\text{norm}}$.

In order to render the position more clear we may draw up a schematic representation of the various levels into which each original level is resolved by the action of the magnetic field. Fig. 31 gives a

[1] The subscripts to the symbols for the term levels here used are based on the inner quantum numbers and are in the reverse order to the ordinary spectroscopic nomenclature (see p. 145).

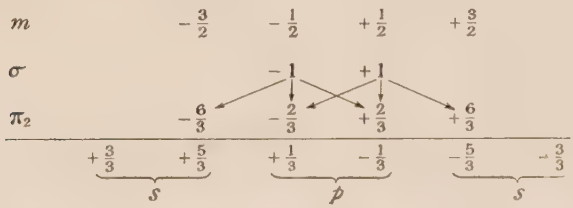
diagram of the magnetic levels for the σ, π_i and δ_i terms, which is self-explanatory when it is remembered that from (25) the maximum value of m for each term is $\pm (I - \frac{1}{2})$, and that the difference between the original energy level and the first magnetic level is $\pm I/r$. In order to determine the Zeeman pattern of any spectrum line it is necessary to take the differences between the magnetic levels of the two spectral terms, the original levels of which combine to give that line. For example the D_2 line is due to the combination $\sigma - \pi_2$ and to obtain the anomalous Zeeman effect as shown by this line we must find the differences between the two magnetic levels of the σ term and the four magnetic levels of the π_2 term, subject to the restrictions set by the selection principle and the rule of polarisation. These may for convenience be once again stated—

$\Delta m = \pm 1$ gives s-components,
$\Delta m = \quad 0$ gives p-components.

In Table CXLIX. are set out the values of the magnetic levels for the σ and π_2 terms.[1]

TABLE CXLIX.

Transition in I, $\Delta I = -1$.



and the arrows indicate those combinations which are permitted by the selection principle. The vertical arrows indicate the transitions for which $\Delta m = 0$ and which give the p-components, whilst the oblique arrows indicate the transitions for which $\Delta m = \pm 1$ and which give the s-components. The values given in the bottom row of the table give the displacements of the components of the magnetically resolved spectrum lines with respect to the undisplaced line in terms of $\Delta \nu_{\text{norm}}$. These displacements are as follows :—

$$p\text{-components} \left\{ \begin{array}{ll} -\frac{2}{3} - (-1) & = +\frac{1}{3} \\ +\frac{2}{3} - 1 & = -\frac{1}{3} \end{array} \right\} = \pm \tfrac{1}{3}$$

$$s\text{-components} \left\{ \begin{array}{ll} +\frac{2}{3} - (-1) & = +\frac{5}{3} \\ +\frac{6}{3} - 1 & = +\frac{3}{3} \\ -\frac{2}{3} - 1 & = -\frac{5}{3} \\ -\frac{6}{3} - (-1) & = -\frac{3}{3} \end{array} \right\} = \pm \tfrac{3}{3}, \quad \pm \tfrac{5}{3}$$

[1] In this table and in all subsequent tables showing the combinations between magnetic levels the transverse Zeeman effect is dealt with, that is to say, the components derived from the combination schemes are always those seen across the lines of force. It is obvious that this is the only method for the proper elucidation of a complete Zeeman pattern.

If we enclose the p-components within brackets the whole Zeeman pattern can be expressed very simply by

$$\frac{\pm (1)\ 3\ 5}{3}$$

it being understood that this is in terms of $\Delta\nu_{\text{norm}}$.

The same method may be applied to all the possible combinations in a doublet system, but before this is done we may consider for a moment the question of the relative intensities of the various Zeeman components. The following rule of intensities has been established as the result of experimental observation, and Landé has given a proof of it by Bohr's correspondence principle.[1]

When two terms combine together which are resolved into a different number of magnetic levels, the strongest p-components are given by the transitions in the centre of the schemes, such as in Table CXLIX., and the strongest s-components are given by the transitions at the extreme ends of the schemes. When two terms combine which are resolved into an equal number of levels the results are reversed, that is to say, the weakest lines are given by the above transitions.

It follows from this rule that in the case of the combination $(\sigma\pi_2)$ set out in Table CXLIX. the strongest s-components will be those with the displacement $\pm\frac{3}{5}$. It happens that in this case there is only one pair of p-components which will be strong. The convention

TABLE CL.

m	$-\frac{1}{2}$	$+\frac{1}{2}$				
σ	-1	$+1$				
π_1	$-\frac{1}{3}$	$+\frac{1}{3}$				
$(\sigma\pi_1)$	$\frac{\pm (2)\ 4}{3}$					

m	$-\frac{5}{2}$	$-\frac{3}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{3}{2}$	$+\frac{5}{2}$
π_2	$-\frac{6}{3}$	$-\frac{2}{3}$	$+\frac{2}{3}$	$+\frac{6}{3}$		
δ_2	$-\frac{15}{5}$	$-\frac{9}{5}$	$-\frac{3}{5}$	$+\frac{3}{5}$	$+\frac{9}{5}$	$+\frac{15}{5}$
$(\pi_2\delta_2)$	$\frac{\pm (1)\ (3)\ 15\ 17\ 19\ 21}{15}$					

m	$-\frac{3}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{3}{2}$	
π_2	$-\frac{6}{3}$	$-\frac{2}{3}$	$+\frac{2}{3}$	$+\frac{6}{3}$	
δ_1	$-\frac{6}{5}$	$-\frac{2}{5}$	$+\frac{2}{5}$	$+\frac{6}{5}$	
$(\pi_2\delta_1)$	$\frac{\pm (4)\ (12)\ 8\ 16\ 24}{15}$				

m	$-\frac{3}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{3}{2}$
π_1	$-\frac{1}{3}$	$+\frac{1}{3}$		
δ_1	$-\frac{6}{5}$	$-\frac{2}{5}$	$+\frac{2}{5}$	$+\frac{6}{5}$
$(\pi_1\delta_1)$	$\frac{\pm (1)\ 11\ 13}{15}$			

[1] *Zeitsch. für Phys.*, **5**, 231 (1921).

has been adopted of expressing the more intense components in heavy type and the Zeeman pattern given by the D_2 line is expressed by

$$\pm\frac{(\mathbf{1})\ \mathbf{3}\ 5}{3}$$

We may now consider the remaining combinations in the doublet system and these are set out in Tables CL. and CLI.

The line $(\pi_1\delta_2)$ does not exist, because the combination involves the transition in the inner quantum number $\Delta 1 = 2$ which, as we have already seen in Chapter I., is forbidden by the selection principle.

The three $(\delta_i\phi_i)$ combinations give the Zeeman resolutions shown in Table CLI.

TABLE CLI.

m	$-\frac{7}{2}$	$-\frac{5}{2}$	$-\frac{3}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{3}{2}$	$+\frac{5}{2}$	$+\frac{7}{2}$
δ_3		$-\frac{15}{5}$	$-\frac{9}{5}$	$-\frac{3}{5}$	$+\frac{3}{5}$	$+\frac{9}{5}$	$+\frac{15}{5}$	
ϕ_4	$-\frac{28}{7}$	$-\frac{20}{7}$	$-\frac{12}{7}$	$-\frac{4}{7}$	$+\frac{4}{7}$	$+\frac{12}{7}$	$+\frac{20}{7}$	$+\frac{28}{7}$
$(\delta_3\phi_4)$	$\pm(\mathbf{1})$	(3)	(5)	**35**	37	39	41	43	45
	35								

m	$-\frac{5}{2}$	$-\frac{3}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{3}{2}$	$+\frac{5}{2}$	
δ_3	$-\frac{15}{5}$	$-\frac{9}{5}$	$-\frac{3}{5}$	$+\frac{3}{5}$	$+\frac{9}{5}$	$+\frac{15}{5}$	
ϕ_3	$-\frac{15}{7}$	$-\frac{9}{7}$	$-\frac{3}{7}$	$+\frac{3}{7}$	$+\frac{9}{7}$	$+\frac{15}{7}$	
$(\delta_3\phi_3)$	$\pm(6)$	(18)	(**30**)	12	24	**36**	48	60
	35							

m	$-\frac{5}{2}$	$-\frac{3}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{3}{2}$	$+\frac{5}{2}$
δ_2	$-\frac{6}{5}$	$-\frac{2}{5}$	$+\frac{2}{5}$	$+\frac{6}{5}$		
ϕ_3	$-\frac{15}{7}$	$-\frac{9}{7}$	$-\frac{3}{7}$	$+\frac{3}{7}$	$+\frac{9}{7}$	$+\frac{15}{7}$
$(\delta_2\phi_3)$	$\pm(\mathbf{1})$	(3)	27	29	31	**33**
	35					

The next system of multiple terms which comes under our notice is the triplet system, and there is no need to deal with the earlier formula which was developed by Landé for the magnetic levels into which each term of this system is resolved. It must be remembered that the later work on spectral series has shown that there are two types of systems, namely, those of even multiplicities, *i.e.* doublet, quartet, etc., systems, and those of uneven multiplicities, *i.e.* singlet,

triplet, etc., systems. This development of spectral theory was dealt with at some length in Chapter I. In view of the fact that Landé has succeeded in finding a complete solution of the problem of the magnetic resolution of every term of any system of multiplicities, it is advisable to omit the intermediate steps and discuss his so-called "g" formula which was obtained, as Sommerfeld says, by a piece of very daring inductive reasoning.

Before proceeding to discuss this g formula we may once again refer to the values of m or equatorial quantum number used in the case of the doublet systems. These were

$$m = \pm \tfrac{1}{2}, \quad \pm \tfrac{3}{2}, \quad \pm \tfrac{5}{2} \ . \ . \ . \pm (\mathrm{I} - \tfrac{1}{2}).$$

The maximum value of m is thus equal to $\pm (\mathrm{I} - \frac{1}{2})$ and the first point we have to notice is that this is perfectly general for all systems of multiplicities. Further, the difference between any two consecutive values of m is equal to unity. In general, therefore, for all systems of multiplicities the values of m are given by

$$m = \pm m_{\max}, \quad \pm (m_{\max} - 1), \quad \pm (m_{\max} - 2), \text{ etc.} \qquad (26)$$

The values of Landé's quantum number I for each of the multiple systems were given on p. 148 and for even multiplicities

$$\mathrm{I} = 1, \ 2, \ 3, \text{ etc.}$$

The values of m for doublet, quartet, sextet, and octet systems are thus half-integral, namely,

$$m = \pm \tfrac{1}{2}, \quad \pm \tfrac{3}{2}, \quad \pm \tfrac{5}{2}, \text{ etc.} \quad . \quad . \quad . \quad (27)$$

For uneven multiplicities we have

$$\mathrm{I} = \tfrac{1}{2}, \ \tfrac{3}{2}, \ \tfrac{5}{2}, \text{ etc.}$$

and consequently $m_{\max}$ is integral and the values of m for singlet, triplet, quintet, and septet systems are also integral, that is to say,

$$m = 0, \quad \pm 1, \quad \pm 2, \quad \pm 3, \text{ etc.} \quad . \quad . \quad (28)$$

In discussing the magnetic resolution of the doublet terms above it was shown that the energy of the magnetic levels can be expressed by

$$\mathrm{W} = \mathrm{W(I)} + mh\frac{2\mathrm{I}}{r}o,$$

where r is the Runge denominator of the term and o is the normal triplet separation. The magnetic levels can therefore be expressed by

$$\frac{\Delta\nu}{o} = m\frac{2\mathrm{I}}{r}.$$

The factor $2I/r$ only applies to the doublet systems and Landé's generalisation states that in any system of multiplicities the magnetic levels are expressed by

$$\frac{\Delta\nu}{o} = mg \quad . \quad . \quad . \quad . \quad . \quad (29)$$

where g is a characteristic constant for each term level and is known as the "resolution factor."

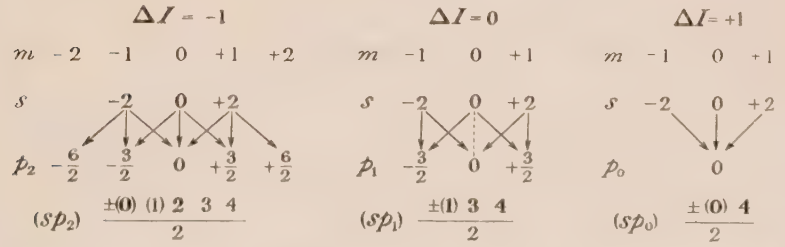
Before dealing with Landé's formula for the calculation of g, we may give the values of this constant for singlet, doublet, and triplet systems, together with the corresponding values of I and $m_{max.}$ These are set forth in Table CLII.

TABLE CLII.

	Singlet			Doublet					Triplet						
Term	S	P	D	σ	π_2	π_1	δ_3	δ_2	s	p_2	p_1	p_0	d_3	d_2	d_1
g	$\frac{0}{0}$	1	1	$\frac{2}{1}$	$\frac{4}{3}$	$\frac{2}{3}$	$\frac{6}{5}$	$\frac{4}{5}$	$\frac{2}{1}$	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{0}{0}$	$\frac{4}{3}$	$\frac{7}{6}$	$\frac{1}{2}$
$m_{max.}$	0	1	2	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$\frac{5}{2}$	$\frac{3}{2}$	1	2	1	0	3	2	1
I	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	1	2	1	3	2	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$\frac{7}{2}$	$\frac{5}{2}$	$\frac{2}{2}$

The values given for doublet systems are the same as those previously used. We may next consider the Zeeman pattern given by spectrum lines belonging to triplet systems and this particularly because an extension of the selection principle or intensity rule must be introduced. The (sp) and (pd) combinations are given in Tables CLIII. and CLIV.

TABLE CLIII.

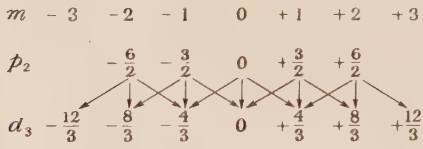


In the case of the (sp_1) combination the p-component, $\Delta\nu = 0$, is missing and it will be seen that this component is given by the transition $m \rightarrow m = 0 \rightarrow 0$ when the transition in I is also zero. As a matter of fact it is always found that the p-component due to the transition $m \rightarrow m = 0 \rightarrow 0$ is always missing when $\Delta I = 0$. We must therefore look on this either as a special extension of the selection principle or alternatively that under this special circumstance the

p-component has zero intensity. This is indicated by the vertical dotted line in the scheme for the (sp_1) combination and the same is done in Table CLIV. for the (p_2d_2) and (p_1d_1) combinations.

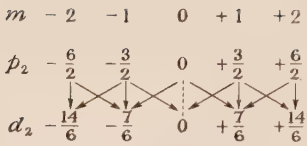
TABLE CLIV.

$\Delta I = -1$



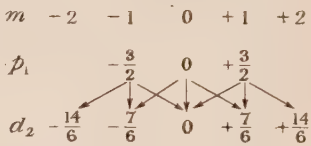
(p_2d_3) $\frac{\pm(0)\ (1)\ (2)\ \mathbf{6}\ 7\ 8\ 9\ 10}{6}$

$\Delta I = 0$



(p_2d_2) $\frac{\pm(2)\ (\mathbf{4})\ 5\ \mathbf{7}\ \mathbf{9}\ 11}{6}$

$\Delta I = -1$

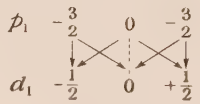


(p_1d_2) $\frac{\pm(\mathbf{0})(2)\ \mathbf{5}\ 7\ 9}{6}$

$\Delta I = +1$

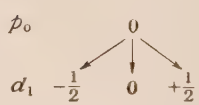
(p_2d_1) $\frac{\pm(\mathbf{0})\ (2)\ 1\ 3\ \mathbf{5}}{2}$

$\Delta I = 0$



(p_1d_1) $\frac{\pm(2)\ \mathbf{1}\ \mathbf{3}}{2}$

$\Delta I = -1$



(p_0d_1) $\frac{\pm(\mathbf{0})\ \mathbf{1}}{2}$

Reference may again be made to the fact which follows generally from Tables CLIII. and CLIV., namely, that the number of magnetic levels into which any spectral term is resolved is always equal to 2I. This is of great importance, since it enables us to determine from observation of the Zeeman effect the value of I for any spectral term, a determination of manifest significance as regards the particular system of multiplicity to which the term belongs. This is far superior to the use of the selection principle as was previously done in the work on multiplet structure described in Chapter I.

If the resolution factor g and the quantum number I were known for every term, we would at once be able to calculate the various magnetic levels mg for every term. With this knowledge at our disposal it will be a simple matter to determine the complete Zeeman pattern for every spectral line with the help of diagrams such as those

TABLE CLV.

$\Delta\nu =$	1	: 2	: 3	: 4	: 5	: 6	: 7		3/2	: 5/2	: 7/2	: 9/2	: 11/2	: 13/2	: 15/2	$= \Delta\nu$
I	1/2	3/2	5/2	7/2	9/2	11/2	13/2	15/2	1	2	3	4	5	6	7	8 = I

Singlet system $R = \frac{1}{2}$

K									K
1/2	0/0								1/2
3/2		1							3/2
5/2			1						5/2
7/2				1					7/2
9/2					1				9/2

Doublet system $R = \frac{2}{2}$

K									K
1/2								2	1/2
3/2							2/3	4/3	3/2
5/2						4/5	6/5		5/2
7/2					6/7	8/7			7/2
9/2				8/9	10/9				9/2

Triplet system $R = \frac{3}{2}$

1/2			2						1/2
3/2	0	3/2	3/2						3/2
5/2		1/2	7/6	4/3					5/2
7/2			2/3	13/12	4/5				7/2
9/2				3/4	21/20	6/5			9/2

Quartet system $R = \frac{4}{2}$

1/2			2						1/2
3/2	8/3	26/15	8/5						3/2
5/2	0	6/5	48/35	10/7					5/2
7/2		2/5	36/35	78/63	4/3				7/2
9/2			4/7	62/63	116/99	14/11			9/2

Quintet system $R = \frac{5}{2}$

1/2			2						1/2
3/2		5/2	11/6	5/3					3/2
5/2	0/0	3/2	3/2	3/2	3/2				5/2
7/2		0	1	5/4	27/20	7/5			7/2
9/2			1/3	11/12	23/30	19/15	4/3		9/2

Sextet system $R = \frac{6}{2}$

1/2				2					1/2
3/2			12/5	66/35	12/7				3/2
5/2	10/3	28/15	58/35	100/63	14/9				5/2
7/2	−2/3	16/15	46/35	88/63	142/99	16/11			7/2
9/2		0	6/7	8/7	14/11	192/143	18/13		9/2

Septet system $R = \frac{7}{2}$

1/2				2					1/2
3/2			7/3	23/12	7/4				3/2
5/2		3	2	7/4	33/20	8/5			5/2
7/2	0	3/2	3/2	3/2	3/2	3/2	3/2		7/2
9/2		−1/2	5/6	7/6	13/30	41/30	59/42	10/7	9/2
K									K

Octet system $R = \frac{8}{2}$

1/2					2				1/2
3/2				16/7	122/63	16/9			3/2
5/2			14/5	72/35	28/21	56/33	18/11		5/2
7/2		4	2	12/7	34/21	52/33	222/143	20/13	7/2
9/2	−4/3	14/15	44/35	86/63	140/99	206/143	284/195	22/15	9/2

I =	1/2	3/2	5/2	7/2	9/2	11/2	13/2	15/2	1	2	3	4	5	6	7	8 = I
$\Delta\nu =$	1	: 2	: 3	: 4	: 5	: 6	: 7		3/2	: 5/2	: 7/2	: 9/2	: 11/2	: 13/2	: 15/2	$= \Delta\nu$

given above. Now Landé shows[1] that the values for g for all the terms of the multiple systems given in Table CLV. on p. 331, that is to say, all the spectral terms of the first order of complexity, may be calculated in a very simple manner from the quantum numbers R, K, and I for each term. The meaning of these numbers was given in Chapter I., p. 146, and may briefly be rehearsed here. R is the quantum number determining the multiplicity of the system, that is to say, $R = \frac{1}{2}, \frac{2}{2}, \frac{3}{2}, \frac{4}{2}$, etc., for singlet, doublet, triplet, quartet, etc., systems. K is Landé's value for the azimuthal quantum number and $K = \frac{1}{2}, \frac{2}{2}, \frac{3}{2}$, etc., for the sharp, principal, diffuse, etc., terms. Landé's formula for g is

$$g = -\frac{3}{2} + \frac{R^2 - K^2}{2(I^2 - \frac{1}{4})} \quad . \quad . \quad . \quad . \quad (30)$$

and this may be written in the form

$$\left.\begin{aligned} g &= 1 + \frac{I^2 - \frac{1}{4}}{2(I^2 - \frac{1}{4})} + \frac{R^2 - \frac{1}{4} - K^2 + \frac{1}{4}}{2(I^2 - \frac{1}{4})} \\ \text{or} \\ g &= 1 + \frac{(I + \frac{1}{2})(I - \frac{1}{2}) + (R + \frac{1}{2})(R - \frac{1}{2}) - (K + \frac{1}{2})(K - \frac{1}{2})}{2(I + \frac{1}{2})(I - \frac{1}{2})} \end{aligned}\right\} \quad (31)$$

In Table CLV. are set forth the complete set of values of the resolution factor g for all the terms of the multiple systems of the first order of complexity, the general form of the table being the same as that of Table LXI. on p. 148.

The values of g given in Table CLV. have all been calculated by means of Landé's formula, and from them the anomalous Zeeman pattern for any spectrum line can be calculated. As an example we may take the line represented by the Landé symbolic method as $n^5_{23} - n^5_{34}$, that is to say, the line $(p_3 d_4)$ of the quintet system. From Table CLV. we obtain the following :—

p_3 $g = \frac{5}{3}$, $I = \frac{7}{2}$, therefore $m_{max} = 3$
d_4 $g = \frac{3}{2}$, $I = \frac{9}{2}$, therefore $m_{max} = 4$

The magnetic levels and the result of their combinations are given in Table CLVI.

TABLE CLVI.

$\Delta I = -1$.

m	−4	−3	−2	−1	0	+1	+2	+3	+4
p_3		$-\frac{15}{3}$	$-\frac{10}{3}$	$-\frac{5}{3}$	0	$+\frac{5}{3}$	$+\frac{10}{3}$	$+\frac{15}{3}$	
d_4	$-\frac{12}{2}$	$-\frac{9}{2}$	$-\frac{6}{2}$	$-\frac{3}{2}$	0	$+\frac{3}{2}$	$+\frac{6}{2}$	$+\frac{9}{2}$	$+\frac{12}{2}$

$(p_3 d_4)$ $\pm$ (0) (1) (2) (3) **6** 7 8 9 10 11 12

6

[1] *Zeitsch. für Phys.*, **15**, 189 (1923); see also E. Back and A. Landé, *Zeemaneffekt und Multiplettstruktur der Spektrallinien*, p. 39, Julius Springer, Berlin, 1925.

As will presently be shown the experimental investigations of Back have proved that the Landé g formula is completely justified.

Before considering Landé's theoretical basis for his formula, we may review Sommerfeld's discussion of the subject, which is of some interest in view of the different values he adopts for the three quantum numbers R, K, and I. In Chapter I. we dealt with his inner quantum number i which is the multiple of the mechanical moment of momentum $ih/2\pi$. To this there corresponds a magnetic moment μ, and the relation between μ and i on the classical theory is given by

$$\mu = i\mu' \quad . \quad . \quad . \quad . \quad . \quad (32)$$

where $\mu' = \frac{e}{m} \cdot \frac{h}{4\pi}$, that is to say, μ' is the fundamental unit of the magnetic moment or the Bohr magneton.

Now the magnetic energy of the atomic state depending on a particular orientation of the atom, if the axis of μ coincides with that of i, can be expressed by [1]

$$\Delta W = \mu H (\cos \mu, H) \quad . \quad . \quad . \quad . \quad (33)$$

that is to say, it is equal to the work which the magnetic field does by the gradual increase in the moment of momentum μ. In order to obtain an expression for this work we must consider the precession of μ with respect to the lines of force, and, remembering what was said above about the axis of μ and the axis of i, we have

$$\cos (\mu, H) = \cos (i, H) = \frac{m}{i} \quad . \quad . \quad . \quad (34)$$

and therefore

$$\Delta W = \frac{\mu}{i} H m. \quad . \quad . \quad . \quad . \quad (35)$$

From this, on division by h, we obtain the magnetic resolution

$$\Delta \nu = \frac{\mu}{i} \cdot \frac{H}{h} m. \quad . \quad . \quad . \quad . \quad (36)$$

If now the resolution be expressed in terms of the normal triplet interval $\Delta \nu_{\text{norm}}$ and μ be expressed in terms of the Bohr magneton, then (36) can be written in the simple form

$$\Delta \nu = \frac{\mu}{i} m. \quad . \quad . \quad . \quad . \quad (37)$$

Equation (37) shows that if the classical relationship holds between μ and i as given in (32) the normal Zeeman triplet only can be obtained, since by substitution in (36) we obtain

$$\Delta \nu = \mu' \frac{H}{h} m = m \Delta \nu_{\text{norm}}.$$

As $\Delta m = 0$ or ± 1, the normal triplet is obtained.

[1] *Ann. der Phys.*, **73**, 209 (1924); see also *Atombau und Spektrallinien*, p. 618.

On the other hand, the true quantum relationship between μ and i which leads to the anomalous Zeeman effect, must be such that μ/i is a rational number which is independent of the principal Bohr quantum number n and the nature of the atom, that is to say, the atomic number. Runge's law, as we have already seen, establishes the fact that μ/i is a rational number, whilst it is evident from Preston's law that this number is independent of n and the atomic number.

Now the rational number μ/i is Landé's resolution factor and we have therefore

$$g = \frac{\mu}{i} \quad . \quad . \quad . \quad . \quad . \quad (38)$$

As can be seen from Table CLV. the value of g for each s term is 2, and consequently, if we write i_s for the value of i for the s term, we have

$$\mu = 2i_s \quad . \quad . \quad . \quad . \quad . \quad (39)$$

that is to say, the magnetic moment of the sharp term is twice the mechanical moment.

Further, for all those atomic states whose values of i are given by summation of i_s and i_a in equal sense,[1] we have

$$\mu = 2i_s + i_a \quad . \quad . \quad . \quad . \quad (40)$$

By division of this last equation by $i = i_s + i_a$ we have

$$g = \frac{\mu}{i} = 2 - \frac{i_a}{i} = 2 - \frac{k-1}{i} \quad . \quad . \quad . \quad (41)$$

There is no doubt from Runge's and Preston's laws that the resolution factor g must be expressed in terms of the quantum numbers r,[2] k, and i. If, as on p. 141, we put

$$k = i_a + 1, \quad r = 2i_s + 1,$$

we can write Landé's g formula as

$$g = 1 + \frac{i(i+1) + i_s(i_s+1) - i_a(i_a+1)}{2i(i+1)} \quad . \quad . \quad (42)$$

This formula can be written as follows:—

$$\begin{aligned} g &= 1 + \frac{i(i+1)}{2i(i+1)} + \frac{{i_s}^2 + i_s - {i_a}^2 - i_a}{2i(i+1)} \\ &= \tfrac{3}{2} + \frac{{i_s}^2 - i_a i_s + i_a i_s - {i_a}^2 + i_s - i_a}{2i(i+1)} \\ &= \tfrac{3}{2} + \tfrac{1}{2}\frac{(i_s - i_a)(i_s + i_a + 1)}{i(i+1)} \quad . \quad . \quad . \quad . \quad (42a) \end{aligned}$$

[1] This means, as was shown on p. 142, that $i = i_{\max} = i_s + i_a$; $i_a = k - 1$.

[2] The meaning of r here used is the permanent multiplicity of the spectral term system (see p. 141).

By substitution in (42*a*) of $i = i_s + i_a$ and subsequent division by $i + 1$, we have

$$g = \tfrac{3}{2} + \tfrac{1}{2}\frac{i_s - i_a}{i_s + i_a} = \frac{2i_s + i_a}{i_s + i_a} \quad . \quad . \quad . \quad (43)$$

whence

$$\mu = ig = 2i_s + i_a.$$

As this is the same result as was obtained above in (40) we find a theoretical basis for Landé's g formula. Sommerfeld gives in his book a table of the values of g for the different levels of the spectral terms calculated from (42*a*), but since these values are the same as those given in Table CLV. they need not be repeated here. Sommerfeld, however, uses his own values of i, i_s, and i_a in place of Landé's I, R, and K.

The development of the theoretical basis as given by Landé for his g formula is somewhat more complicated. The symmetrical formula given in (31), namely,

$$g = 1 + \frac{(I + \tfrac{1}{2})(I - \tfrac{1}{2}) + (R + \tfrac{1}{2})(R - \tfrac{1}{2}) - (K + \tfrac{1}{2})(K - \tfrac{1}{2})}{2(I + \tfrac{1}{2})(I - \tfrac{1}{2})}$$

may be written in the form

$$g = 1 + \frac{\bar{I}^2 + \bar{R}^2 - \bar{K}^2}{2\bar{I}^2} \quad . \quad . \quad . \quad (44)$$

where $\bar{I}$ stands for the geometric mean $\sqrt{(I + \tfrac{1}{2})(I - \tfrac{1}{2})}$ and R and K have similar meanings. Now (44) may be expressed as

$$g = \frac{\bar{I} + R\,(\cos RI)}{\bar{I}} \quad . \quad . \quad . \quad . \quad (45)$$

and can be interpreted as follows. The magnetic levels mg, if we put $\cos(IH) = \cos\theta = m/\bar{I}$ (compare equation (35) above), have the values

$$\Delta\nu = omg = o\bar{I}\cos\bar{\theta} + o\bar{R}\cos\bar{\theta}\cos(\bar{R}\bar{I}) \quad . \quad . \quad (46)$$

where $o = \Delta\nu_{\text{norm}}$.

In the case of the normal triplet, where $g = 1$, we have

$$\Delta\nu_{\text{norm}} = om = o\bar{I}\cos\bar{\theta} \quad . \quad . \quad . \quad (47)$$

By the precession of R and K with respect to I and the simultaneous precession of I with respect to H we have the mean values

$$\overline{\cos(\bar{R}, H)} = \cos(\bar{R}, \bar{I}) \,.\, \cos(\bar{I}, H) = \cos(\bar{R}, \bar{I})\cos\bar{\theta}$$
$$\overline{\cos(\bar{K}, H)} = \cos(\bar{K}, \bar{I}) \,.\, \cos(\bar{I}, H) = \cos(\bar{K}, \bar{I})\cos\bar{\theta}$$

and equations (46) and (47) pass over into

$$\left.\begin{aligned} \Delta\nu &= omg = o[\bar{K} \,.\, \overline{\cos(\bar{K}, H)} + 2\bar{R} \,.\, \overline{\cos(\bar{R}, H)}] \\ \text{and} \quad \Delta\nu_{\text{norm}} &= om = \;[\bar{K} \,.\, \overline{\cos(\bar{K}, H)} + \bar{R} \,.\, \overline{\cos(\bar{R}, H)}] \end{aligned}\right\} \quad . \quad (48)$$

It follows from these equations that the abnormal Zeeman effect is connected with the fact that the atomic trunk has double the value of magnetic energy as in the normal case. This is the same conclusion as that arrived at by Sommerfeld's reasoning in equations (39) and (40). This statement is the same as that the Larmor precession of the atoms in the magnetic field is not equal to o but to og.

Landé says that there remains unexplained the necessity for the use of the geometrical means $\bar{R}$, $\bar{K}$, and I in place of the values R, K, and I which were previously employed. Furthermore, the use of half-integral quantum numbers for R, K, and I would seem to break through the fundamental principle of the quantum theory. On the other hand, the use of half integral quantum numbers is equally forced on us by the phenomena of emission band spectra, as will be discussed in Chapter IV. The most recent observations of Curtis would seem to require quarter-integral quantum numbers for their explanation. Whilst this latter conception might seem to be somewhat *ad hoc*, the half-integral values are definitely justified. At the present state of development of our insight into these atomic phenomena, it does not seem that the half-integral values of quantum numbers need cause undue concern. The essential feature of the whole is the quantum jump, not the size of the initial and final quantum numbers, and in all the scales of quantum numbers employed by Landé or by Sommerfeld the quantum jump is always integral or zero.

Turning once again to the values of the resolution factor g given in Table CLV. there are one or two interesting points which are worthy of consideration.

In the first place, we find in the uneven systems of multiplicities the following four conditions in Sommerfeld's notation :—

Singlet	$i = 0$	$i_a = i_s = 0$	s term,
Triplet	$i = 0$	$i_a = i_s = 1$	p term,
Quintet	$i = 0$	$i_a = i_s = 2$	d term,
Septet	$i = 0$	$i_a = i_s = 3$	f term.

In all four the value of g is indeterminate and is given as $\frac{0}{0}$.

Again, in the even multiplicities we find that $g = 0$ for the d_1 term of the quartet system and the g_2 term of the sextet system. When a line due to the combination of any two of these terms is examined in the magnetic field it shows no Zeeman effect whatsoever.

In the second place, we have in the uneven systems of multiplicities the condition in Sommerfeld's notification that $i_s = i_a$. As can be seen at once from equation (42a) this at once leads to $g = \frac{3}{2}$, which therefore is true for all the levels (except the first where $i = 0$) in the particular horizontal row.

In the third place, attention may be drawn to the fact that the average value of g in any horizontal row of the table is equal to 1 when the permanent number of multiplicities has been reached, and

equal to 2 when the number of terms is less than the permanent number. This may be illustrated by the quartet system, thus

s term	$g = 2$.
p terms	sum of three values of $g = \frac{8}{3} + \frac{26}{15} + \frac{8}{5} = \frac{90}{15} = 6$, Average, $g = 2$.
d terms	sum of four values of $g = 0 + \frac{6}{5} + \frac{48}{35} + \frac{10}{7} = 4$, Average, $g = 1$.
f terms	sum of four values of $g = \frac{2}{5} + \frac{36}{35} + \frac{78}{65} + \frac{4}{3} = 4$, Average, $g = 1$.
g terms	sum of four values of $g = \frac{4}{7} + \frac{62}{65} + \frac{116}{99} + \frac{14}{11} = 4$, Average, $g = 1$.

This was first pointed out by Heisenberg,[1] and will be discussed in greater detail below.

We may now consider the application of the g formula to the experimental observation of the anomalous Zeeman effect, and for this we are indebted to Back.[2] This investigation established beyond question the validity of Landé's g formula and, as was shown in Chapter I., p. 149, proved that the terms functioning in the arc spectrum of manganese belong to systems of even multiplicities, and that the terms functioning in the spark spectrum belong to systems of uneven multiplicities.

The problem before us is the determination from a given Zeeman resolution picture of the values of I and g for the two terms, the combination of which gives the original undisturbed spectrum line. It is convenient to use the conventional integral values of i in place of those of I which are half-integral for the systems of uneven multiplicities. This convention was dealt with in Chapter I., p. 147, where it was shown that $i = \mathrm{I}$ for even multiplicities, and $i = \mathrm{I} - \frac{1}{2}$ for uneven multiplicities. We have already seen that the equatorial quantum number m takes the values

$m = \pm\frac{1}{2}, \quad \pm\frac{3}{2}, \quad \pm\frac{5}{2} \ldots (\mathrm{I} - \frac{1}{2})$ for even multiplicities.
$m = \pm 0, \quad \pm 1, \quad \pm 2 \ldots (\mathrm{I} - \frac{1}{2})$ for uneven multiplicities.

It follows at once that

$$\left.\begin{aligned} m_{\max} + \tfrac{1}{2} &= i \text{ for even multiplicities} \\ m_{\max} &= i \text{ for uneven multiplicities} \end{aligned}\right\} \quad \ldots \quad (49)$$

The half-integral values of m for even multiplicities lead to the distribution of the p-components of the resolved line in the series 1, 3, 5, etc., whilst the integral values of m for uneven multiplicities lead to their distribution in the series 0, 1, 2, etc. This can be seen in Table CLI for the $(\delta_i\phi_i)$ lines of the doublet system and in Table CLVI. for the (p_3d_4) line of the quintet system.

In addition to this we have the information given by the intensity

[1] *Zeitsch. für Phys.*, **8**, 273 (1922). [2] *Ibid.*, **15**, 206 (1923).

rules of Landé (see p. 326) which may again be stated here. The two terms which combine to give the original line may be called x and y and their values of i and g may be denoted by i_x, g_x and i_y, g_y, respectively. Then

(*a*) If $i_x \neq i_y$, the strongest p-components lie nearest to the centre of the Zeeman pattern and the strongest s-components are given by the combination of the magnetic terms $g_x \times \pm m_{\max}$ and $g_y \times \pm m_{\max}$.

(*b*) If $i_x = i_y$, the outermost p-components are the most intense, and the strongest s-components are formed by combinations between the magnetic levels mg_x and mg_y which are in the centre of the combination scheme, such as shown in Table CLIV. Further, in this case the central p-component, $\Delta\nu = 0$, has zero intensity in uneven systems.

It will be seen from these general relations that there must be a limited number of fundamental types of Zeeman patterns with respect to symmetry relations and distribution of intensity. Every Zeeman pattern conforms to one of these types and only differs from its fundamental type in the number of its components and the magnitude of the separation of the components. Since there are four quantities concerned, namely i_x, i_y, g_x, g_y, it would be expected that there would be nine of these fundamental types determined by the following conditions :—

1 $\begin{cases} g_x > g_y \\ i_x > i_y \end{cases}$	2 $\begin{cases} g_x > g_y \\ i_x = i_y \end{cases}$	3 $\begin{cases} g_x > g_y \\ i_x < i_y \end{cases}$
4 $\begin{cases} g_x = g_y \\ i_x > i_y \end{cases}$	5 $\begin{cases} g_x = g_y \\ i_x = i_y \end{cases}$	6 $\begin{cases} g_x = g_y \\ i_x < i_y \end{cases}$
7 $\begin{cases} g_x < g_y \\ i_x > i_y \end{cases}$	8 $\begin{cases} g_x < g_y \\ i_x = i_y \end{cases}$	9 $\begin{cases} g_x < g_y \\ i_x < i_y \end{cases}$

It is obvious, however, that these are not all different because the two terms x and y are interchangeable. Clearly the following pairs are identical, 1 and 9, 2 and 8, 3 and 7, and 4 and 6, with the result that the possibilities are reduced to five, which may be written as follows :—

1 $\begin{cases} i_x > i_y \\ g_x > g_y \end{cases}$	2 $\begin{cases} i_x > i_y \\ g_x = g_y \end{cases}$	3 $\begin{cases} i_x > i_y \\ g_x < g_y \end{cases}$
4 $\begin{cases} i_x = i_y \\ g_x \neq g_y \end{cases}$	5 $\begin{cases} i_x = i_y \\ g_x = g_y \end{cases}$	

These five conditions lead to ten fundamental types, namely, five for even multiplicities and five for uneven multiplicities. The necessity for differentiating between the two types given by the same i and g relation is rendered sufficiently obvious by what was said above as regards the separation ratios of the p-components.

A further simplification becomes possible if we consider the two i and g relations given in 2 and 5, in both of which $g_x = g_y$. In Table CLVII. are given the four combination schemes for the two

relations in the systems of even and uneven multiplicities, and in each case we may put $g_x = g_y = 4/3$.

TABLE CLVII.

Uneven systems

$i_x = i_y + 1$

m	-2	-1	0	$+1$	$+2$
mg_x	$-\frac{8}{3}$	$-\frac{4}{3}$	0	$+\frac{4}{3}$	$+\frac{8}{3}$
mg_y		$-\frac{4}{3}$	0	$+\frac{4}{3}$	

Type $= \frac{\pm(0)\ 4}{3} = \pm(0)\, g$

$i_x = i_y$

m	-1	0	$+1$
mg_x	$-\frac{4}{3}$	0	$+\frac{4}{3}$
mg_y	$-\frac{4}{3}$	0	$+\frac{4}{3}$

Type $= \frac{\pm(0)\ 4}{3} = \pm(0)\, g$

Even systems

$i_x = i_y + 1$

m	$-\frac{3}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{3}{2}$
mg_x	$-\frac{6}{3}$	$-\frac{2}{3}$	$+\frac{2}{3}$	$+\frac{6}{3}$
mg_y		$-\frac{2}{3}$	$+\frac{2}{3}$	

Type $= \frac{\pm(0)\ 4}{3} = \pm(0) g$

$i_x = i_y$

m	$-\frac{3}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{3}{2}$
mg_x	$-\frac{6}{3}$	$-\frac{2}{3}$	$+\frac{2}{3}$	$+\frac{6}{3}$
mg_y	$-\frac{6}{3}$	$-\frac{2}{3}$	$+\frac{2}{3}$	$+\frac{6}{3}$

Type $= \frac{\pm(0)\ 4}{3} = \pm(0) g$

In each of the four schemes there results a Zeeman triplet with two s-components separated by $\pm g$ from a central p-component with $\Delta\nu = 0$. It is perhaps worth mentioning that in the uneven systems when $i_x = i_y$ the central p-component is not given by the transition $m \to m = 0 \to 0$, which is forbidden by the special rule, but by the transitions $\Delta m = 0$ when $m = 1, 2, 3$, etc.

It follows from this that the two i, g relations given under 2 and 5 only give one type which is common to both even and uneven systems. The total number of fundamental types is therefore seven and these may be described in detail. The numbering of the types finally adopted by Back is set forth in Table CLVIII.

TABLE CLVIII.

Type 1	$\begin{cases} i_x \geq i_y \\ g_x < g_y \end{cases}$	Type 2	$\begin{cases} i_x \geq i_y \\ g_x > g_y \end{cases}$	Type 3	$\begin{cases} i_x = i_y \\ g_x \neq g_y \end{cases}$ All for uneven multiplicities.
Type 4	$\begin{cases} i_x \geq i_y \\ g_x < g_y \end{cases}$	Type 5	$\begin{cases} i_x \geq i_y \\ g_x > g_y \end{cases}$	Type 6	$\begin{cases} i_x = i_y \\ g_x \neq g_y \end{cases}$ All for even multiplicities.

Type 7 $\begin{cases} i_x = i_y \\ g_x = g_y \end{cases}$ for both even and uneven multiplicities.

Type 7 also is given by the relations of Types 1 and 2 in the limiting case when $i_y = 0$.

In Table CLIX. are given the combination schemes, together with

diagrams, showing the total number of components and their intensity distribution. In these diagrams the upper vertical lines represent the p-components, and the lower vertical lines represent the s-components, the length of these lines indicating intensity. In the combination schemes only those combinations are indicated by arrows which give the most intense s-components, these being the most important for the purposes of calculation of the four quantities i_x, i_y, g_x, g_y. For the sake of simplicity the same values of g have been used in all the tables, namely, $g = \frac{6}{5}$ or $\frac{7}{5}$.

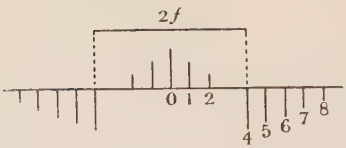
TABLE CLIX.

Type 1.

$i_x = i_y + 1, \quad g_x < g_y.$

m	-3	-2	-1	0	$+1$	$+2$	$+3$
mg_x	$-\frac{18}{5}$	$-\frac{12}{5}$	$-\frac{6}{5}$	0	$+\frac{6}{5}$	$+\frac{12}{5}$	$+\frac{18}{5}$
mg_y		$-\frac{14}{5}$	$-\frac{7}{5}$	0	$+\frac{7}{5}$	$+\frac{14}{5}$	

$$\pm \frac{(0)(1)(2)\ 4\ 5\ 6\ 7\ 8}{5}$$

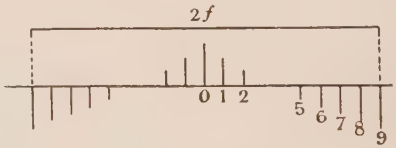


Type 2.

$ix = i_y + 1 \quad g_x > g_y.$

m	-3	-2	-1	0	$+1$	$+2$	$+3$
mg_x	$-\frac{21}{5}$	$-\frac{14}{5}$	$-\frac{7}{5}$	0	$+\frac{7}{5}$	$+\frac{14}{5}$	$+\frac{21}{5}$
mg_y		$-\frac{12}{5}$	$-\frac{6}{5}$	0	$+\frac{6}{5}$	$+\frac{12}{5}$	

$$\pm \frac{(0)(1)(2)\ 5\ 6\ 7\ 8\ 9}{5}$$

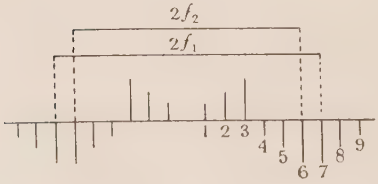


Type 3.

$i_x = i_y, \quad g_x \neq g_y.$

m	-3	-2	-1	0	$+1$	$+2$	$+3$
mg_x	$-\frac{18}{5}$	$-\frac{12}{5}$	$-\frac{6}{5}$	0	$+\frac{6}{5}$	$+\frac{12}{5}$	$+\frac{18}{5}$
mg_y	$-\frac{21}{5}$	$-\frac{14}{5}$	$-\frac{7}{5}$	0	$+\frac{7}{5}$	$+\frac{14}{5}$	$+\frac{21}{5}$

$$\pm \frac{(1)(2)(3)\ 4\ 5\ 6\ 7\ 8\ 9}{5}$$

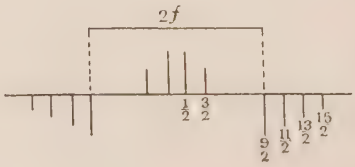


Type 4.

$i_x = i_y + 1, \quad g_x < g_y.$

m	$-\frac{5}{2}$	$-\frac{3}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{3}{2}$	$+\frac{5}{2}$
mg_x	$-\frac{15}{5}$	$-\frac{9}{5}$	$-\frac{3}{5}$	$+\frac{3}{5}$	$+\frac{9}{5}$	$+\frac{15}{5}$
mg_y		$-\frac{21}{10}$	$-\frac{7}{10}$	$+\frac{7}{10}$	$+\frac{21}{10}$	

$$\pm \frac{(1)(3)9\ 11\ 13\ 15}{10}$$



Type 5.

$i_x = i_y + 1, \quad g_x > g_y.$

m	$-\frac{5}{2}$	$-\frac{3}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{3}{2}$	$+\frac{5}{2}$
mg_x	$-\frac{35}{10}$	$-\frac{21}{10}$	$-\frac{7}{10}$	$+\frac{7}{10}$	$+\frac{21}{10}$	$+\frac{35}{10}$
mg_y		$-\frac{9}{5}$	$-\frac{3}{5}$	$+\frac{3}{5}$	$+\frac{9}{5}$	

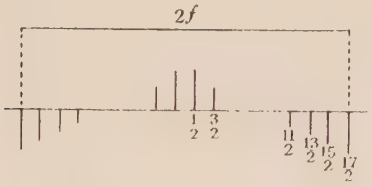
$$\frac{\pm (1)(3)\ 11\ 13\ 15\ 17}{10}$$

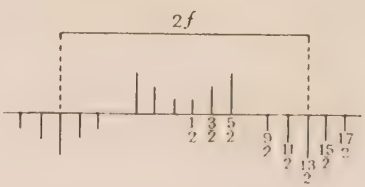
Type 6.

$i_x = i_y, \quad g_x \neq g_y.$

m	$-\frac{5}{2}$	$-\frac{3}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{3}{2}$	$+\frac{5}{2}$
mg_x	$-\frac{35}{10}$	$-\frac{21}{10}$	$-\frac{7}{10}$	$+\frac{7}{10}$	$+\frac{21}{10}$	$+\frac{35}{10}$
mg_y	$-\frac{15}{5}$	$-\frac{9}{5}$	$-\frac{3}{5}$	$+\frac{3}{5}$	$+\frac{9}{5}$	$+\frac{15}{5}$

$$\frac{\pm (1)(3)(5)\ 9\ 11\ 13\ 15\ 17}{10}$$





Type 7 has already been shown in Table CLVII. so far as the relation $\left\{\begin{matrix} i_x = i_y \\ g_x = g_y \end{matrix}\right\}$ is concerned. The limiting case of $\left\{\begin{matrix} i_x > i_y \\ g_x \neq g_y \end{matrix}\right\}$ when $g_y = 0$ or $i_y = 0$ is shown in the following scheme :—

m	-1	0	1,
mg_x	$-\frac{6}{5}$	0	$+\frac{6}{5}$,
mg_y		0	

$$\frac{\pm (0)(6)}{5} \quad \text{or} \quad \pm (0)g.$$

A comparison of the intensity distribution of the components in the first six types shows that the three pairs 1 and 4, 2 and 5, 3 and 6 have quite different intensity relations. The two types in each pair can at once be differentiated by the different spacing of the p-components. One of the two types in each pair is always an uneven multiplicity, the other being an even multiplicity. As stated above, the components in the former are spaced in the series 0, 1, 2, etc., and in the latter in the series 1, 3, 5, etc. This is most easy to recognise in the p-components.

In order to determine the values of i_x, i_y, g_x, and g_y we can make use of certain simple relations which can be seen to exist from the above schemes. Thus in

Types 1, 2, 4, 5 $g_x - g_y = \pm e$ which gives the spacing of the components.

$i_x g_x - i_y g_y = \pm f =$ the distance of the most intense s-component from the undisturbed line.

Type 3 $g_x - g_y = \pm (f_2 - f_1) = \pm e$

$g_x = f_1$

$g_y = f_2$.

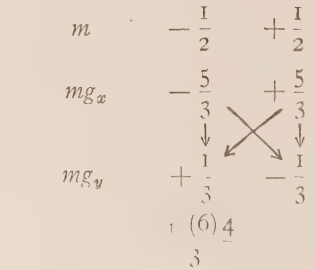
Type 6 $g_x - g_y = \pm e$

$\frac{g_x}{2} + \frac{g_y}{2} = \pm f$.

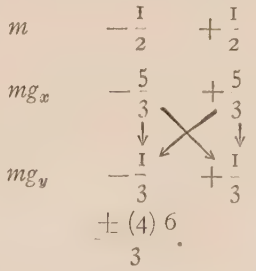
Back says that with a good photograph of the Zeeman pattern there is no doubt as to the fundamental type to which the pattern conforms. Further, the determination of the values of i_x, i_y, g_x, and g_y can be made when the type is known, except in the rare case of a magnetic triplet where ambiguity arises as to the value of i due to $i_y = 0$ or $g_y = 0$. As a matter of fact it is possible in practice to remove all doubt by use of Landé's table of values of g.

The fundamental types 1, 2, 4, and 5 often appear as pseudo-triplets when the values of g_x and g_y are not very different, for in this case e is very small. For the same reasons Types 3 and 6 often appear as pseudo-quartets. This, however, introduces no special difficulty, since the intensity distribution leads to the recognition of the actual type. These pseudo-types will be dealt with in fuller detail below.

There still remains the possibility that g_x or g_y may have a negative value, three such negative values being given in Landé's table, namely $-\frac{2}{3}$, $-\frac{1}{2}$, and $-\frac{4}{3}$ for the terms $n^6_{4\text{I}}$, $n^7_{5\text{I}}$, and $n^8_{5\text{I}}$ respectively. Back found such a case in his investigation of the arc spectrum of manganese in the line $\lambda = 3839{\cdot}777$, which will be referred to below. This line is due to the combination $n^6_{4\text{I}} - n^6_{3\text{I}}$ or $d_1 - f_1$. As will be seen from Landé's table $g_x = \frac{10}{3}$ and $g_y = -\frac{2}{3}$, and as we are dealing with the combination of two terms in a system of even multiplicities (sextet) we have the following scheme of combination between two magnetic levels :—



On the other hand, if g_y had been $+\frac{2}{3}$ the Zeeman resolution would have been given by



It is obvious that the first case is the reverse of the second, and as the second is the normal (the separation of the p-components less than that of the s-components) the first case, due to either g_x or g_y being negative, is called an inverted type.

We may now deal with Back's detailed observations of the magnetic resolution of the lines of the arc and spark spectra of manganese in order to understand the method of determining the values of i and g for each term which functions in the emission of a spectrum line. Before these details are set forth reference must be made to the Paschen-Back effect, which will be described below. The necessity for mentioning this phenomenon at this point is due to the fact that in the examination of the Zeeman effect exhibited by the lines of a simple or complex multiplet we frequently find the Zeeman pattern of a line to be distorted owing to the influence of a neighbouring line, that is to say, an incipient Paschen-Back effect. Although this does not interfere with the recognition of the fundamental type to which the affected line belongs, yet it introduces a complication into the measurements of the components of the Zeeman pattern given by that line.

Several of the manganese lines give distorted Zeeman resolutions, but it must be understood that the evidence afforded by the undisturbed lines observed by Back was of itself sufficiently strong to prove the validity of Landé's g values and also, as will be shown later, it is possible to make corrections for the asymmetry shown by the disturbed lines. The discussion of this correction and its method of application may be postponed, for it is always advisable in dealing with a notable advance of knowledge such as this not to confuse the issue by discussing corrections necessary in certain cases, provided that the evidence in the majority of cases is sufficiently free from doubt to justify an assertion as to the truth of the theory we have set out to prove. The theory at the moment under review is the Landé g formula and Back has certainly succeeded in establishing its correctness. For this reason we may consider his evidence without any undue anxiety as to those lines which show badly distorted Zeeman patterns. That the asymmetry must be dealt with

is obvious for the benefit of those who wish to work in this field, but we may for the moment accept it as a disagreeable fact, and return to it when the confidence caused by Back's measurements is secured.

In the measurement of any spectrum photograph such as that of a Zeeman pattern, the first measurements are naturally expressed in some unit of linear measure on the photographic negative. In the present case these must then be converted into terms of the normal triplet separation, since the Landé g values are of course fractions of that interval. In order to do this it is necessary to determine the strength of the magnetic field operating when the Zeeman pattern was photographed. The method of determination of H will be dealt with in the experimental section below. The linear measurements made of the components of the Zeeman pattern are first expressed in terms of $\Delta\lambda$ with reference to the position of the undisturbed line and at this point the corrections for the distortion are introduced. These values of $\Delta\lambda$ are then converted to wave-numbers and finally expressed in terms of the normal triplet interval.

Back lays considerable stress on the advisability of expressing these fractions in decimal notation and not as vulgar fractions. There are two reasons in favour of this. In the first place, it is thereby rendered easier to avoid any bias in favour of one or other value of g, which is always expressed as a vulgar fraction. In the second place, in determining the value of g_x and g_y from the Zeeman patterns shown by the lines of a complex multiplet, it will generally be found that more than one value of each will be obtained. The means of the various values of g_x and g_y, expressed in decimal notation, will lead to far more accurate determinations of g_x and g_y than would be obtained by attempting to express each value of g_x and g_y as a vulgar fraction in the first instance.

The first group of lines in the arc spectrum of manganese examined by Back was the triplet at

$$\lambda = 4823{\cdot}522$$
$$4783{\cdot}432$$
$$4754{\cdot}048,$$

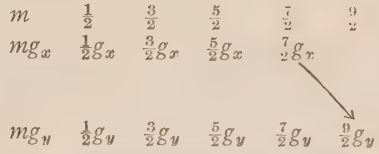
and the following results were obtained :—

$\lambda = 4823{\cdot}522$, Zeeman pattern completely resolved.

Observed values $\pm$ (*0·1108*) (0·3324) (0·5540) (0·7756) *0·9973* 1·219 1·441 1·662 1·884 . . .

The three outermost s-components were too faint to measure, but all the p-components were capable of accurate measurement and therefore afford the necessary information as to the complete resolution. The intensity distribution is such that both p- and s-components fall in intensity outwards from the centre of the picture. Clearly, therefore, Type 1 or 4 is present and, since the components lie in the series 1, 3, 5, 7, etc., we are able to conclude without any doubt that we have in this case Type 4. Since there are four p-components on each

side of the centre it is obvious that there are four magnetic levels for one term and five for the other. The scheme of combination of the magnetic levels must therefore be as follows if only one half of the scheme is indicated :—



where the oblique arrow indicates the combination giving the most intense *s*-component.

In the first place, we have in the case of the x term $m_{\max} = \pm \frac{7}{2}$ and in the case of the y term $m_{\max} = \pm \frac{9}{2}$, whence by equation (49) we find that $i_x = 4$ and $i_y = 5$.

In the second place, we have the following arithmetical relations :—

$$\begin{aligned} \tfrac{7}{2}g_x - \tfrac{7}{2}g_y &= \quad 0{\cdot}7756 \\ \tfrac{7}{2}g_x - \tfrac{9}{2}g_y &= -0{\cdot}9973 \end{aligned}$$

$$\text{whence} \quad \begin{cases} g_y = 1{\cdot}773 \\ g_x = 1{\cdot}995 \end{cases}$$

Now the values of g_y and g_x, expressed as rational numbers are very nearly $\frac{16}{9}$ and $\frac{2}{1}$, respectively, since $\frac{16}{9} = 1{\cdot}778$. The difference between the rational numbers and the calculated values of g_y and g_x is $-0{\cdot}3$ per cent., and we can express this by $\Delta g_y = \Delta g_x = -0{\cdot}3$ per cent. Assuming the rational numbers to be correct the components of the Zeeman pattern expressed in decimal fractions are

$$\pm (0{\cdot}111)\ (0{\cdot}333)\ (0{\cdot}555)\ (0{\cdot}778)\ 1{\cdot}00\ 1{\cdot}22\ 1{\cdot}44\ 1{\cdot}66\ 1{\cdot}89\ 2{\cdot}11\ 2{\cdot}33\ 2{\cdot}55.$$

$\lambda = 4783{\cdot}432$. This line gave a Zeeman pattern which is markedly distorted by the previous line and the *s*-components only were completely resolved, there being seven of these on each side of the centre. The measurements were

$$\pm \ldots\ (0{\cdot}211)\ 1{\cdot}785\ 1{\cdot}845\ 1{\cdot}905\ 1{\cdot}966\ 2{\cdot}026\ 2{\cdot}087\ 2{\cdot}147.$$

The intensity distribution of the *p*-components was such that the intensity increases from the centre outwards, and in the case of the *s*-components the most intense line is in the centre of each group. We have, therefore, Type 6, and $i_x = i_y = 4$, since i_y must be less than i_y for the previous line by unity. As can be seen from the first and third lines of this triplet $g_x = 2$ and therefore g_x must also be 2 for this line.

We have $\frac{1}{2}g_x + \frac{1}{2}g_y = 1{\cdot}966$ and therefore $g_y = 1{\cdot}932$. The nearest rational number to this is $\frac{29}{15} = 1{\cdot}933$, but we also have $\frac{122}{63} = 1{\cdot}937$. The choice between these two rational numbers cannot be made from the measurements and we may leave the choice over until the third

line of the triplet has been considered. Note may be made of the experimental errors which are

$$\begin{matrix} {}^{2}{}_{1}{}^{9}{}_{5} & \Delta g_y = -0{\cdot}05 \text{ per cent.} \\ {}^{1}{}_{6}{}^{2}{}_{3}{}^{2} & \Delta g_y = -0{\cdot}25 \text{ per cent.} \end{matrix}$$

On the assumption that $g_y = {}^{1}{}_{6}{}^{2}{}_{3}{}^{2}$ the calculated separations of the components are

$$\pm (0{\cdot}032)\ (0{\cdot}095)\ (0{\cdot}158)\ (\textit{0·222})\ 1{\cdot}778\ 1{\cdot}840\ 1{\cdot}904\ \textit{1·968}\ 2{\cdot}031\ 2{\cdot}094\ 2{\cdot}158.$$

$\lambda = 4754{\cdot}058$. This line was completely resolved and the following measurements of the components were obtained :—

$$\pm (\textit{0·143})\ (0{\cdot}429)\ (0{\cdot}716)\ \textit{1·278}\ 1{\cdot}565\ 1{\cdot}851\ 2{\cdot}173\ \ldots,$$

the two outermost s-components being too weak to measure. The distributions of the intensities and the spacing of the components give definite evidence in favour of Type 4. Obviously therefore the combination scheme is as follows, since there are three p-components :—

m	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$
mg_x	$\frac{1}{2}g_x$	$\frac{3}{2}g_x$	$\frac{5}{2}g_x$	$\frac{7}{2}g_x$
mg_y	$\frac{1}{2}g_y$	$\frac{3}{2}g_y$	$\frac{5}{2}g_y$	

It follows that $i_x = 4$ and $i_y = 3$, the most intense s-component being given by $\frac{7}{2}g_x - \frac{5}{2}g_y$. We thus have

$$\begin{matrix} \frac{5}{2}g_x - \frac{3}{2}g_y = -0{\cdot}716 \\ \frac{7}{2}g_x - \frac{5}{2}g_y = \quad \textit{1·278} \end{matrix}$$

$$\text{that is to say} \quad \begin{cases} g_x = 1{\cdot}994 \\ g_y = 2{\cdot}280. \end{cases}$$

In rational numbers $g_x = \frac{2}{1}$, $\Delta g_x = -0{\cdot}3$ per cent.

$$g_y = \frac{1}{7}^{6} = 2{\cdot}286, \quad \Delta g_y = -0{\cdot}3 \text{ per cent.}$$

The problem is now completely solved since the triplet consists of three lines, the two outer lines of which are formed by the combination of a term with $i = 4$ and $g = \frac{2}{1}$ with two terms having $i = 5$, $g = \frac{1}{7}^{6}$ and $i = 3$, $g = \frac{1}{9}^{6}$, respectively, whilst the central line is due to the combination between the term having $i = 4$, $g = \frac{2}{1}$ with a term having $i = 4$, $g = {}^{2}{}_{1}{}^{9}{}_{5}$ or ${}^{1}{}_{6}{}^{2}{}_{3}{}^{2}$. It is obvious, apart from any other reasoning, that the triplet must be a principal triplet (sp_i) and we know that the terms belong to the system of even multiplicities. There can be no doubt that the triplet is a member of an octet system since $i = 4$ for the s term. If we use the value $g = {}^{1}{}_{6}{}^{2}{}_{3}{}^{2}$ for the middle line of the triplet we have the values set forth in Table CLX.

TABLE CLX.

i	3	4	5		
g_x		2		n^8_{14}	
g_y	$\frac{16}{7}$	$\frac{122}{63}$	$\frac{16}{9}$	n^8_{2i}	$i = 3, 4, 5.$

and these values of g are identical with those given by Landé for the s term and three p terms of the octet system.

We may now take the narrow triplet of manganese at

$$\lambda = 4030{\cdot}760$$
$$4033{\cdot}074$$
$$4034{\cdot}489.$$

$\lambda - 4030{\cdot}760$. This line was completely resolved and the measurements of the components were

$$\pm (0{\cdot}142)\ (0{\cdot}426)\ (0{\cdot}710)\ 0{\cdot}994\ 1{\cdot}278\ 1{\cdot}562\ 1{\cdot}846\ 2{\cdot}130\ 2{\cdot}414$$

The intensity distribution and the spacing of the components show that the Zeeman pattern conforms to Type 4. There are three p-components on each side of the centre and consequently $m_{\max}$ for the y term is $\pm \frac{7}{2}$ and for the x term $\pm \frac{5}{2}$, the values of i_y and i_x being 4 and 3 respectively. Clearly therefore

$$\tfrac{5}{2}g_x - \tfrac{5}{2}g_y = 0{\cdot}710$$
$$\tfrac{5}{2}g_x - \tfrac{7}{2}g_y = -\,0{\cdot}994,$$

whence $\begin{cases} g_y = 1{\cdot}704, & \text{that is } \frac{1{\cdot}2}{7} = 1{\cdot}714, \quad \Delta g_y = -\,0{\cdot}6 \text{ per cent.} \\ g_x = 1{\cdot}988, & \text{that is } \frac{2}{1}, \quad \Delta g_x = -\,0{\cdot}5 \text{ per cent.} \end{cases}$

Calculated values,

$$\pm (0{\cdot}143)\ (0{\cdot}429)\ (0{\cdot}715)\ 1{\cdot}00\ 1{\cdot}287\ 1{\cdot}573\ 1{\cdot}862\ 2{\cdot}145\ 2{\cdot}424.$$

$\lambda = 4033{\cdot}074$. The Zeeman pattern of this line was very unsymmetrical and the p-components were not fully resolved. The measurements were

$$\pm (0{\cdot}251)\ 1{\cdot}700\ 1{\cdot}830\ 1{\cdot}945\ 2{\cdot}070\ 2{\cdot}190,$$

and the intensity distribution indicated Type 6, and the number of the s-components proved that $i_x = i_y = 3$.

For the same reason as in the case of the previous triplet we know that g_x is again 2 for this line, and since

$$\tfrac{1}{2}g_x + \tfrac{1}{2}g_y = 1{\cdot}945$$

we have $g_y = 2 \times 1{\cdot}945 - 2 = 1{\cdot}890$. The nearest rational number to this is $\frac{17}{9} = 1{\cdot}889$, but the value $\frac{66}{55} = 1{\cdot}886$ ($\Delta = 0{\cdot}4$ per cent.) is very nearly as good.

$\lambda = 4034{\cdot}489$. This line was completely resolved into the following components

$$\vdash (0{\cdot}1997)\ (0{\cdot}5991)\ 1{\cdot}412\ 1{\cdot}811\ 2{\cdot}210\ 2{\cdot}609.$$

Clearly therefore this conforms to Type 4 and, since there are two p-components on each side of the centre, $i_x = 3$ and $i_y = 2$. We thus have

$$\tfrac{5}{2}g_x - \tfrac{3}{2}g_y = 1{\cdot}412$$
$$\tfrac{3}{2}g_x - \tfrac{3}{2}g_y = -0{\cdot}599,$$

whence $\begin{cases} g_x = 2{\cdot}011, \text{ that is } \frac{2}{1}, & \Delta g_x = +0{\cdot}05 \text{ per cent.} \\ g_y = 2{\cdot}399, \text{ that is } \frac{12}{5} = 2{\cdot}40, & \Delta g_y = -0{\cdot}05 \text{ per cent.} \end{cases}$

The values of g_x and g_y are assembled in Table CLXI.

TABLE CLXI.

i	2	3	4		
g		2		n^6_{13}	
g	$\frac{12}{5}$	$\frac{66}{35}$	$\frac{12}{7}$	n^6_{2i}	$i = 2, 3, 4,$

and as the triplet belongs to a system of even multiplicities this must be the sextet system since $i = 3$ for the sharp term. The values of g are identical with those given in Landé's table.

Of the four manganese arc multiplets examined by Back we may first select for discussion the one of 14 lines having the following wave-lengths :—

λ.	λ.
3776·537*	3823·896
3790·215	3829·674
3799·256*	3833·864
3806·866*	3834·363
3809·599	3839·777
3816·746*	3841·081
3823·515	3843·985.

This multiplet was attributed to the combination (D_1F_1) by Sommerfeld (see p. 140). In the case of the lines marked with an asterisk Back was unable to determine the Zeeman pattern.

$\lambda = 3809{\cdot}599$. Completely resolved with the following measurements : —

$\pm$ (0·1124) (0·2990) (0·4856) (*0·6722*) 0·940 1·128 1·314 *1·501* 1·688 1·874 2·061.

This clearly conforms to Type 6 in spite of the fact that the spacing of the p-components is not exactly on the series 1, 3, 5, etc. We have, therefore, $g_x/2 + g_y/2 = 1{\cdot}501$, whilst the four p-components are given by $(g_x/2 - g_y/2) \times 1$, 3, 5, and 7, respectively. The most accurate value will be obtained from the most intense p-component that is 0·6722. We thus have

$$\frac{g_x}{2} - \frac{g_y}{2} = 0{\cdot}096 = \frac{0{\cdot}6722}{7},$$

and since $$\frac{g_x}{2} + \frac{g_y}{2} = 1{\cdot}501,$$

we have $$\begin{cases} g_x = 1{\cdot}597 \\ g_y = 1{\cdot}405. \end{cases}$$

The nearest rational numbers to these values are

$$g_x = \tfrac{8}{5} = 1{\cdot}600$$
$$g_y = \tfrac{7}{5} = 1{\cdot}400.$$

Now the number of p-components is 4 and the Type is No. 6, consequently we have without any ambiguity $i_x = i_y = 4$. The fact that there are only 14 lines in this multiplet indicates that it is due to the combination of a five-membered term with a six-membered term which argues in favour of the (df) combination in the sextet system. This is confirmed by the Zeeman resolution of the remaining lines, and in particular of the line $\lambda = 3829{\cdot}674$. Now the values of g given by Landé for the d_4 and f_4 terms of the sextet system are 100/63 and 88/63, respectively. We may therefore provisionally adopt these values for g_y and g_x, for they are not very different from the calculated values, thus

$$g_x = \tfrac{100}{63} = 1{\cdot}587, \qquad \Delta g_x = +\,0{\cdot}7 \text{ per cent.}$$
$$g_y = \tfrac{88}{63} = 1{\cdot}397, \qquad \Delta g_y = +\,0{\cdot}5 \text{ per cent.}$$

These give the following calculated values :—

$\pm$ (0·095) (0·286) (0·476) (*0·666*) 0·921 1·111 1·302 *1·492* 1·682 1·873 2·063.

$\lambda = 3823{\cdot}515$. Completely resolved, but the s-components overlap those of the line at $\lambda = 3823{\cdot}896$ without, however, any partial Paschen-Back effect in either case. The measurements were

$\pm$ (*0·0764*) (0·229) (0·382) (0·535) *0·901* 1·053 1·206 1·359 1·512 1·665 . . .

This pattern obviously conforms to Type 4, and the presence of four p-components establishes that $i_x = 4$ and $i_y = 5$. We have therefore

$$\tfrac{7}{2}g_x - \tfrac{7}{2}g_y = 0{\cdot}5347$$
$$\tfrac{7}{2}g_x - \tfrac{9}{2}g_y = -\,0{\cdot}9010.$$

whence $$\begin{cases} g_y = 1{\cdot}4357 \\ g_x = 1{\cdot}588 \end{cases}$$

The simplest rational numbers are

$$g_y = \tfrac{10}{7} = 1{\cdot}429, \qquad \Delta g_y = +\,0{\cdot}4 \text{ per cent.}$$
$$g_x = \tfrac{8}{5} = 1{\cdot}60, \qquad \Delta g_x = -\,0{\cdot}6 \text{ per cent.}$$

The Landé value for g_x provisionally adopted for the preceding line is far closer to the calculated value since

$$g_x = \tfrac{100}{63} = 1{\cdot}587, \qquad \Delta g_x = +\,0{\cdot}08 \text{ per cent.}$$

Similarly g_y can be better expressed by the Landé value 142/99 since

$$g_y = \tfrac{142}{99} = 1{\cdot}434, \qquad \Delta g_y = +\,0{\cdot}15 \text{ per cent.}$$

These values of g_x and g_y give the following spacing of the components

$\pm$ (*0·0765*) (0·229) (0·362) (0·535) *0·899* 1·052 1·205 1·358 1·511 1·664 1·817 1·970,

which are practically identical with Back's measurements. The simpler rational numbers $\frac{10}{7}$ and $\frac{8}{5}$ do not give any agreement with observation, the calculated position of the components being

$\pm$ (*0·08571*) (0·2571) (0·4285) (0·600) *0·828* 1·000 1·172 1·344 . . .

The value of $g_x = 100/63$, provisionally adopted in the case of the first line, is thus completely verified.

$\lambda = 3823{\cdot}896$. Completely resolved, the measurements being

$\pm$ (0·173) (0·520) (*0·866*) 0·787 1·133 *1·479* 1·825 2·171.

Once again we have Type 6, and hence, since there are three p-components, $i_x = i_y = 3$. The arithmetical relations are

$$\tfrac{1}{2}g_x - \tfrac{1}{2}g_y = 0{\cdot}173$$
$$\tfrac{1}{2}g_x + \tfrac{1}{2}g_y = 1{\cdot}479,$$
$$\text{therefore} \quad g_x = 1{\cdot}652,$$
$$\text{and} \quad g_y = 1{\cdot}306.$$

The Landé values of g for n^6_{43} and n^6_{23} are $\frac{58}{35}$ and $\frac{46}{35}$, respectively, and these are very near to the calculated values. Thus

$$g_x = \tfrac{58}{35} = 1{\cdot}657, \qquad \Delta g_x = -\,0{\cdot}3 \text{ per cent.}$$
$$g_y = \tfrac{46}{35} = 1{\cdot}314, \qquad \Delta g_y = -\,0{\cdot}6 \text{ per cent.}$$

The position of the components as calculated from these values are

$\pm$ (0·171) (1·513) (*0·857*) 0·798 1·142 *1·486* 1·830 2·174

$\lambda = 3829{\cdot}674$. All the components were measured and were found to have the following values :—

0·605 (*1·262*) *3·128*.

The Zeeman pattern is thus Type 5 inverted, which means that g_y has a negative value. As there is only one p-component and $i_x = i_y + 1$, it follows that $i_x = 2$ and $i_y = 1$. We thus have

$$\tfrac{1}{2}g_x - \tfrac{1}{2}g_y = 1{\cdot}262$$
$$\tfrac{3}{2}g_x - \tfrac{1}{2}g_y = 3{\cdot}128,$$

therefore

$$\begin{cases} g_x = 1{\cdot}866, & \text{that is } \frac{28}{15} = 1{\cdot}867, \\ g_y = -0{\cdot}658, & \text{that is } -\frac{2}{3} = -0{\cdot}667, \quad \Delta g_y = -1{\cdot}3 \text{ per cent.} \end{cases}$$

There is no possible doubt that g_y is negative, for in no other way can the inversion of the type be explained. It will be understood that less accuracy is to be expected owing to the small number of the components. It is possible too that some magnetic disturbance accounts for the comparatively large error in the determination of g_y. This establishment of the negative value is of great importance since in Landé's table of g values there are three negative values of g, each with $i = 1$. Two of these occur in the systems of even multiplicities, namely, the terms n^6_{41} with $g = -\frac{2}{3}$ and n^8_{51} with $g = -\frac{4}{3}$. The octet system is ruled out since the multiplet would then have been due to the combination (F_4G_4) with 20 lines. The evidence therefore is overwhelmingly strong in favour of the (DF) combination in the sextet system. In view of what was said above about the resolution of this line the deviation between the observed value of g_y and Landé's value of $-\frac{2}{3}$ is not serious. The calculated position of the components is

$$\pm 0{\cdot}600 \ (\textit{1·266}) \ \textit{3·133}.$$

$\lambda = 3833{\cdot}864$. The components of this line partly overlap those of the next line, $\lambda = 3834{\cdot}363$, with a decrease in the accuracy of measurement. No partial Paschen-Back effect was noticed in either case. The measurements were

$$\pm (0{\cdot}398) \ (\textit{1·194}) \ 0{\cdot}648 \ \textit{1·444} \ 2{\cdot}240.$$

This conforms to Type 6, and since there are two p-components we have $i_x = i_y = 2$. It follows that

$$\begin{aligned} \tfrac{1}{2}g_x - \tfrac{1}{2}g_y &= 0{\cdot}398 \\ \tfrac{1}{2}g_x + \tfrac{1}{2}g_y &= 1{\cdot}444, \end{aligned}$$

and therefore

$$\begin{cases} g_x = 1{\cdot}842, \text{ that is } \frac{28}{15} = 1{\cdot}867, & \Delta g_x = -1 \text{ per cent.} \\ g_y = 1{\cdot}046, \text{ that is } \frac{16}{15} = 1{\cdot}066, & \Delta g_y = -2 \text{ per cent.} \end{cases}$$

The calculated position of the components is

$$\pm (0{\cdot}400) \ 0{\cdot}666 \ (\textit{1·20}) \ \textit{1·466} \ 2{\cdot}266.$$

$\lambda = 3834{\cdot}363$. The remarks made in connection with the previous line must be noted. The measurements were

$$\pm (\textit{0·1297}) \ (0{\cdot}3891) \ (0{\cdot}6485) \ \textit{0·7393} \ 0{\cdot}9988 \ 1{\cdot}258 \ 1{\cdot}518 \ldots$$

Clearly this conforms to Type 4 and as there are three p-components $i_x = 3$ and $i_y = 4$. We thus have

$$\tfrac{5}{2}g_x - \tfrac{5}{2}g_y = 0{\cdot}6485$$
$$\tfrac{5}{2}g_x - \tfrac{7}{2}g_y = -\,0{\cdot}7393,$$

and $\begin{cases} g_y = 1{\cdot}388, & \text{that is, } \frac{8}{6}\frac{8}{3} = 1{\cdot}397, \quad \Delta g_y = -\,0{\cdot}6 \text{ per cent.} \\ g_x = 1{\cdot}647, & \text{that is, } \frac{5}{3}\frac{8}{5} = 1{\cdot}657, \quad \Delta g_x = -\,0{\cdot}6 \text{ per cent.} \end{cases}$

The calculated positions of the components are

$$\pm\,(0{\cdot}1302)\ (0{\cdot}3905)\ (0{\cdot}6508)\ 0{\cdot}7460\ 1{\cdot}006\ 1{\cdot}276\ 1{\cdot}527\ 1{\cdot}787\ 2{\cdot}047.$$

$\lambda = 3839{\cdot}777$. The Zeeman pattern of this line is Type 6 inverted. The measurements were

$$\pm\,1{\cdot}337\ (1{\cdot}987).$$

There being only one p-component it follows that $i_x = i_y = 1$ and

$$\tfrac{1}{2}g_x - \tfrac{1}{2}g_y = 1{\cdot}987$$
$$\tfrac{1}{2}g_x + \tfrac{1}{2}g_y = 1{\cdot}337,$$

therefore

$$\begin{cases} g_x = 3{\cdot}324, & \text{that is, } \frac{1}{3}^{0} = 3{\cdot}333, \quad \Delta g_x = -\,0{\cdot}3 \text{ per cent.} \\ g_y = -\,0{\cdot}650, & \text{that is, } -\frac{2}{3} = -\,0{\cdot}667, \quad \Delta g_y = -\,2{\cdot}8 \text{ per cent.} \end{cases}$$

These rational numbers give the following positions of the components

$$\pm\,1{\cdot}333\ (2{\cdot}000).$$

The large deviation in the case of g_y can be explained by the poor accuracy of measurement with only four components altogether.

$\lambda = 3841{\cdot}081$. Completely resolved. The components had the positions

$$\pm\,(0{\cdot}2794)\ 0{\cdot}4831\ (0{\cdot}8316)\ 1{\cdot}037\ 1{\cdot}592\ 2{\cdot}146,$$

and this conforms to Type 4 with $i_x = 2$ and $i_y = 3$. Consequently we have

$$\tfrac{3}{2}g_x - \tfrac{3}{2}g_y = 0{\cdot}8316$$
$$\tfrac{3}{2}g_x - \tfrac{5}{2}g_y = -\,0{\cdot}4831,$$

and

$$\begin{cases} g_y = 1{\cdot}315, \text{ that is } \frac{4}{3}\frac{6}{5} = 1{\cdot}314, & \Delta g_y = +\,0{\cdot}07 \text{ per cent.} \\ g_x = 1{\cdot}869, \text{ that is } \frac{2}{1}\frac{8}{5} = 1{\cdot}867, & \Delta g_x = +\,0{\cdot}1 \text{ per cent.} \end{cases}$$

These values give

$$\pm\,(0{\cdot}2762)\ 0{\cdot}4857\ (0{\cdot}8286)\ 1{\cdot}038\ 1{\cdot}590\ 2{\cdot}143.$$

$\lambda = 3843{\cdot}985$. Completely resolved. The components had the positions

$$\pm\,0{\cdot}076\ (1{\cdot}135)\ 2{\cdot}199.$$

This conforms to Type 4 with $i_x = 1$ and $i_y = 2$, and we have

$$\tfrac{1}{2}g_x - \tfrac{1}{2}g_y = 1{\cdot}135$$
$$\tfrac{1}{2}g_x + \tfrac{1}{2}g_y = 2{\cdot}199,$$

whence

$$\begin{cases} g_x = 3{\cdot}324, \text{ that is } \frac{10}{3} = 3{\cdot}333, & \Delta g_x = -\,0{\cdot}3 \text{ per cent.} \\ g_y = 1{\cdot}074, \text{ that is } \frac{16}{15} = 1{\cdot}067, & \Delta g_y = +\,0{\cdot}7 \text{ per cent.} \end{cases}$$

These values give

$$\pm 0{\cdot}067 \quad (1{\cdot}133) \quad 2{\cdot}200.$$

The following two lines could only be examined qualitatively.

$\lambda = 3790{\cdot}215$. This gives a pseudo-quartet of Type 6 although the separate components were too faint to measure. The only possible measurements, though not accurate, were

$$\pm \ldots \quad (0{\cdot}586) \quad \ldots \quad 1{\cdot}460.$$

It is evident from the type that $i_x = i_y$ and the consideration of the other lines in the multiplet leads to the value $i_x = i_y = 5$. We have already found that g_y for $i = 5$ is $\frac{142}{99}$ from the line $\lambda = 3823{\cdot}515$. The best solution obtainable from the above measures is

$$g_x = 1{\cdot}52, \qquad \frac{14}{9} = 1{\cdot}55$$
$$g_y = 1{\cdot}402, \qquad \frac{142}{99} = 1{\cdot}434.$$

These values give

$$\pm \ldots \quad (0{\cdot}545) \quad \ldots \quad 1{\cdot}494.$$

$\lambda = 3806{\cdot}866$. This gives a pseudo-triplet of Type 4 but the components were not capable of measurement. If the values found for g_x and g_y are assembled together they can be seen to agree with those for the d and f terms of a sextet system, as shown by Table CLXII.

TABLE CLXII.

i	1	2	3	4	5	6		
g_x	$\frac{10}{3}$	$\frac{28}{15}$	$\frac{58}{35}$	$\frac{100}{63}$	$\left[\frac{14}{9}\right]$		n^6_{3i}	$i = 1, 2, 3, 4, 5.$
g_y	$-\frac{2}{3}$	$\frac{16}{15}$	$\frac{46}{35}$	$\frac{88}{63}$	$\frac{142}{99}$	$\left[\frac{16}{11}\right]$	n^6_{4i}	$i = 1, 2, 3, 4, 5, 6.$

The value $\frac{14}{9}$ for n^6_{35} has been found by Back from another multiplet and consequently is correct. The value $\frac{16}{11}$ for n^6_{46} has not been as yet observed since the line in which this term occurs is $\lambda = 3806{\cdot}866$, the Zeeman components of which, as stated above, could not be measured.

The details of Back's measurements of the two multiplets at $\lambda = 4084 - 4018$ and $\lambda = 3630 - 3578$ need not be given. It is, however, of importance that we consider a fourth multiplet which was not observed by Catalan, but was discovered by Back. This new multiplet consists of eight lines, having the following wave-lengths: —

λ.	Int.	ν
4235·125	8	23605·43
4235·306	10	23604·41
4239·723	7	23579·83
4257·653	8	23480·53
4265·920	9	23435·03
4281·097	9	23351·95
4284·084	3	23335·68
4312·546	2	23181·66

The Zeeman resolution of all these lines was observed with the following results :—

$\lambda = 4235{\cdot}125$. Completely resolved, with partial overlapping by the components of the next line. The measurements were

$$\pm (0{\cdot}163)\ (0{\cdot}489)\ 0{\cdot}890\ 1{\cdot}216\ 1{\cdot}542\ 1{\cdot}868.$$

These conform to Type 4, and consequently $i_x = 2$ and $i_y = 3$. We have, therefore,

$$\tfrac{5}{2}g_y - \tfrac{3}{2}g_x = 0{\cdot}890$$
$$\tfrac{3}{2}g_y - \tfrac{3}{2}g_x = -0{\cdot}489,$$

whence

$$\begin{cases} g_y = 1{\cdot}379, & \text{that is } \frac{48}{35} = 1{\cdot}371, \quad \Delta g_y = +0{\cdot}06 \text{ per cent.} \\ g_x = 1{\cdot}705, & \text{that is } \frac{26}{15} = 1{\cdot}733, \quad \Delta g_x = -1{\cdot}7 \text{ per cent.} \end{cases}$$

These two values of g belong to the quartet system, and though the value of g_x is not very accurate, this conclusion is amply confirmed by the Zeeman pattern of the remaining lines. The calculated position of the components are

$$\pm (0{\cdot}162)\ (0{\cdot}486)\ 0{\cdot}886\ 1{\cdot}210\ 1{\cdot}533\ 1{\cdot}856.$$

$\lambda = 4235{\cdot}306$. Completely resolved, with some overlapping by the previous line. Type 4, as the following measurements prove :—

$$\pm (0{\cdot}0865)\ (0{\cdot}2595)\ (0{\cdot}4325)\ 0{\cdot}995\ 1{\cdot}168\ 1{\cdot}341\ 1{\cdot}514\ \ldots$$

There being three p-components, $i_x = 3$ and $i_y = 4$, and consequently we have

$$\tfrac{7}{2}g_y - \tfrac{5}{2}g_x = 0{\cdot}995$$
$$\tfrac{5}{2}g_y - \tfrac{5}{2}g_x = -0{\cdot}4325.$$

whence $\begin{cases} g_y = 1{\cdot}4275, \text{ that is } \frac{10}{7} = 1{\cdot}4286 \\ g_x = 1{\cdot}6000, \text{ that is } \frac{8}{5}. \end{cases}$

The calculated positions of the components are

$$\pm (0{\cdot}0857)\ (0{\cdot}257)\ (0{\cdot}429)\ 1{\cdot}000\ 1{\cdot}171\ 1{\cdot}343\ 1{\cdot}514\ 1{\cdot}686\ 1{\cdot}857.$$

$\lambda = 4239{\cdot}723$. Completely resolved. Type 4, as the following measurements prove :—

$$\pm 0{\cdot}4623\ (0{\cdot}7356)\ 1{\cdot}895,$$

and therefore we have $i_x = i$ and $i_y = 2$. Consequently

$$\tfrac{3}{2}g_y - \tfrac{1}{2}g_x = 0{\cdot}4623$$
$$\tfrac{1}{2}g_y - \tfrac{1}{2}g_x = -0{\cdot}7356.$$

whence $\begin{cases} g_y = 1{\cdot}1979, \text{ that is } \frac{6}{5} = 1{\cdot}200 \\ g_x = 2{\cdot}6691, \text{ that is } \frac{8}{3} = 2{\cdot}667, \end{cases}$

the calculated positions of the components being

$$\pm\, 0{\cdot}467 \quad (0{\cdot}733) \quad 1{\cdot}933.$$

$\lambda = 4257{\cdot}653$. This is an interesting case since there are on each side of the centre of the Zeeman pattern one p- and one s-component having identical positions, namely,

$$\dashv \quad (1{\cdot}332) \quad 1{\cdot}332.$$

This is a special case of Type 6 with $i_x = i_y = 1$, since there is only one component of each kind. It is clear that

$$\tfrac{1}{2}g_x + \tfrac{1}{2}g_y = 1{\cdot}332$$
$$\tfrac{1}{2}g_x - \tfrac{1}{2}g_y = 1{\cdot}332,$$

whence $\begin{cases} g_x = 2{\cdot}664, \text{ that is } \frac{8}{3} = 2{\cdot}667. \\ g_y = 0. \end{cases}$

These values of g_x and g_y give for the calculated positions of the components

$$\pm\, (1{\cdot}333) \quad 1{\cdot}333.$$

$\lambda = 4265{\cdot}920$. Type 6, with the following measurements :—

$$\pm \ldots \quad (0{\cdot}794) \quad 0{\cdot}926 \quad 1{\cdot}456 \quad 1{\cdot}986.$$

There being two p-components we have $i_x - i_y = 2$, and further

$$\tfrac{1}{2}g_x + \tfrac{1}{2}g_y = 1{\cdot}456$$
$$\tfrac{3}{2}g_x - \tfrac{1}{2}g_y = 1{\cdot}986,$$

whence $\begin{cases} g_x = 1{\cdot}721, \text{ that is } \frac{26}{15} = 1{\cdot}733 \\ g_y = 1{\cdot}192, \text{ that is } \frac{6}{5} = 1{\cdot}20. \end{cases}$

The calculated positions of the components are

$$\pm\, (0{\cdot}267) \quad (0{\cdot}800) \quad 0{\cdot}933 \quad 1{\cdot}467 \quad 2{\cdot}000.$$

$\lambda = 4281{\cdot}097$. Completely resolved into Type 6, the measurements being

$$\pm\, (0{\cdot}1113) \quad (0{\cdot}3375) \quad (0{\cdot}5637) \quad 1{\cdot}030 \quad 1{\cdot}256 \quad 1{\cdot}482 \quad 1{\cdot}709 \quad 1{\cdot}935.$$

Since there are three p-components we have $i_x = i_y = 3$. Now it is obvious that the measurements of these p-components are not good, since they do not fall accurately into the series 1, 3, 5 as they should. We can, however, obtain the values of g_x and g_y from the s-components as follows :—

$$\begin{aligned} \tfrac{5}{2}g_y + \tfrac{5}{2}g_x &= 5 \times 1{\cdot}482 = 7{\cdot}410 \\ \tfrac{5}{2}g_y - \tfrac{3}{2}g_x &= 1{\cdot}030. \end{aligned}$$

whence $\begin{cases} g_x = 1{\cdot}595, \text{ that is } \frac{8}{5} = 1{\cdot}600 \\ g_y = 1{\cdot}369, \text{ that is } \frac{48}{35} = 1{\cdot}371. \end{cases}$

These values of g_x and g_y give the following calculated positions of the components

$$\pm (0{\cdot}1143)\ (0{\cdot}3429)\ (\textit{0·5715})\ 1{\cdot}029\ 1{\cdot}257\ \textit{1·486}\ 1{\cdot}714\ 1{\cdot}943.$$

$\lambda = 4284{\cdot}084$. Completely resolved into Type 5 and similar to the case of $\lambda = 4257{\cdot}653$ in that the p-component and one of the s-components have identical positions, the measurements being

$$\pm (\textit{0·861})\ 0{\cdot}861\ \textit{2·575}.$$

This case differs from the previous case in that there are two s-components and consequently we have $i_x = 2$ and $i_y = 1$ and $g_x > g_y$. It is further certain that $g_y = 0$ from the above pattern. The simplest way to obtain g_x is from the p-component which gives

$$\begin{cases} g_x = 2 \times 0{\cdot}861 = 1{\cdot}722, \text{ that is } \frac{26}{15} = 1{\cdot}733 \\ g_y = 0. \end{cases}$$

We have for the calculated position of the components

$$\pm (\textit{0·867})\ 0{\cdot}867\ \textit{2·601}.$$

$\lambda = 4312{\cdot}546$. Completely resolved into Type 5, but the components were very faint. The measurements were

$$\pm (\textit{0·206})\ (0{\cdot}618)\ 1{\cdot}385\ 1{\cdot}797\ \textit{2·209}.$$

It is obvious from this pattern that $i_x = 3$ and $i_y = 2$ and that $g_x > g_y$. We have therefore

$$\begin{aligned} \tfrac{5}{2}g_x - \tfrac{3}{2}g_y &= 2{\cdot}209 \\ \tfrac{3}{2}g_x - \tfrac{3}{2}g_y &= 0{\cdot}618, \end{aligned}$$

whence $\begin{cases} g_x = 1{\cdot}591, & \text{that is } \frac{8}{5} = 1{\cdot}60 \\ g_y = 1{\cdot}180, & \text{that is } \frac{6}{5} = 1{\cdot}20. \end{cases}$

The calculated values are

$$\pm (\textit{0·2})\ (0{\cdot}6)\ 1{\cdot}0\ 1{\cdot}4\ 1{\cdot}8\ \textit{2·2}.$$

The values of g_x and g_y found from this multiplet are collected in Table CLXIII. and as can be seen they agree with those calculated by Landé for the p and d terms of the quartet system.

TABLE CLXIII.

i	1	2	3	4		
g_x	$\frac{8}{3}$	$\frac{26}{15}$	$\frac{8}{5}$		n^4_{2i}	$i = 1, 2, 3.$
g_y	0	$\frac{6}{5}$	$\frac{48}{35}$	$\frac{10}{7}$	n^4_{3i}	$i = 1, 2, 3, 4.$

We may now turn to the spark spectrum of manganese and consider the Zeeman resolutions of the two triplets and one of the multiplets discovered by Catalan.[1]

Triplet at

$\lambda = 2949{\cdot}207$
$\lambda = 2939{\cdot}315$
$\lambda = 2933{\cdot}066.$

$\lambda = 2949{\cdot}207$. Completely resolved, with the following measurements :—

$$\pm (0)\ (0{\cdot}336)\ (0{\cdot}672)\ \mathit{0{\cdot}995}\ 1{\cdot}331\ 1{\cdot}667\ 2{\cdot}003\ \ldots$$

As can be seen from the intensity distribution it conforms to either Type 1 or Type 4, and as the components are spaced in the series 0, 1, 2, 3, etc., the Type present is No. 1. This triplet therefore belongs to a system of uneven multiplicities. The combination scheme between the magnetic levels is now shown by

m	0	1	2	3
mg_x	0	g_x	$2g_x$	
mg_y	0	g_y	$2g_y$	$3g_y$

and we have therefore

$$2g_x - 2g_y = 0{\cdot}672.$$
$$2g_x - 3g_y = -0{\cdot}995.$$

whence $\begin{cases} g_y = 1{\cdot}667, & \text{that is } \frac{5}{3} = 1{\cdot}667 \\ g_x = 2{\cdot}003, & \text{that is } \frac{2}{1}. \end{cases}$

Since by (49) on p. 337 $m_{\max} = i$ for uneven multiplicities, we have $i_x = 2$ and $i_y = 3$. The fact that $g = 2$ for $i = 2$ for the x term suggests that we have here a principal triplet (sp_i) of a quintet system, and this is confirmed by the observations of the other two lines.

The calculated values of the components are

$$\pm (0)\ (0{\cdot}333)\ (0{\cdot}667)\ \mathit{1{\cdot}000}\ 1{\cdot}333\ 1{\cdot}667\ 2{\cdot}000\ 2{\cdot}333.$$

$\lambda = 2939{\cdot}315$. Not completely resolved, but the pattern was recognised as conforming to Type 3 and consequently $i_x = i_y$. The measurements were

$$\ldots\ (\mathit{0{\cdot}331})\ \ldots\ \mathit{1{\cdot}837}\ \mathit{2{\cdot}01}\ \ldots$$

Now it is evident from the combination scheme

m	0	1	2
mg_x	0	g_x	$2g_x$
mg_y	0	g_y	$2g_y$

[1] See Chap. I., p. 132.

that the two most intense s-components give directly the value of g_x and g_y. We thus have

$g_x = 2{\cdot}01$, that is $\frac{2}{1}$

$g_y = 1{\cdot}837$, that is $\frac{11}{6} = 1{\cdot}833$, $\Delta g_y = +0{\cdot}2$ per cent.

The first p-component, the component 0 being absent since $i_x = i_y$, is given by $g_x - g_y = 2{\cdot}000 - 1{\cdot}833 = 0{\cdot}167$ and the second by 0·334. The most intense p-component is thus given by $2g_x - 2g_y$ and consequently $i_x = i_y = 2$. The calculated positions of the components are

(0·167) (*0·333*) 1·667 *1·833 2·000* 2·167.

$\lambda = 2933{\cdot}066$. Completely resolved and conforms to Type 1, the measurements being

$\pm$ (*0*) (0·501) *1·490* 1·991 2·492.

Here we have two p-components, including the one at 0, and we see at once that $i_x = 1$ and $i_y = 2$. The values of g_x and g_y are found from the combination scheme

m	0	1	2
mg_x	0	g_x	$2g_x$
mg_y	0	g_y	

whence

$$2g_x - g_y = 1{\cdot}490$$
$$g_x - g_y = -0{\cdot}501,$$

and

$g_x = 1{\cdot}991$, that is $\frac{2}{1}$,

$g_y = 2{\cdot}492$, that is $\frac{5}{2} = 2{\cdot}5$, $\Delta g_y = -0{\cdot}32$ per cent.

The calculated positions of the components are

$\pm$ (*0*) (0·5) *1·5* 2·0 2·5.

The values of g_x and g_y for the triplet are assembled in Table CLXIV.

TABLE CLXIV.

i	1	2	3		
g_x		2		n^5_{12}	
g_y	$\frac{5}{2}$	$\frac{11}{6}$	$\frac{5}{3}$	n^5_{2i}	$i = 1, 2, 3.$

These values agree absolutely with those given by Landé for the quintet system in his Table on p. 331.

Second triplet at

$\lambda = 2576{\cdot}116$

$\lambda = 2593{\cdot}734$

$\lambda = 2605{\cdot}695.$

$\lambda = 2576{\cdot}116$. Completely resolved and conforms to Type 1. The measurements were

$$\pm (0)\ (0{\cdot}248)\ (0{\cdot}496)\ (0{\cdot}744)\ \textit{0·992}\ 1{\cdot}240\ 1{\cdot}488\ 1{\cdot}736\ \ldots$$

From the number of p-components it is evident that $i_x = 3$ and $i_y = 4$. The values of g_x and g_y are found from

$$3g_x - 3g_y = 0{\cdot}744$$
$$3g_x - 4g_y = -\,0{\cdot}992.$$

whence

$$\begin{cases} g_y = 1{\cdot}736, & \text{that is } \frac{7}{4} = 1{\cdot}75, \quad \Delta g_y = -\,0{\cdot}8 \text{ per cent.} \\ g_x = 1{\cdot}984, & \text{that is } \frac{2}{1}, \quad\ \ \Delta g_x = -\,0{\cdot}8 \text{ per cent.} \end{cases}$$

The calculated values are

$$\pm (0)\ (0{\cdot}25)\ (0{\cdot}50)\ (0{\cdot}75)\ \textit{1·00}\ 1{\cdot}25\ 1{\cdot}50\ 1{\cdot}75\ 2{\cdot}00\ 2{\cdot}25\ 2{\cdot}50.$$

$\lambda = 2593{\cdot}734$. Distorted and not completely resolved, the only measurements given by Back being

$$\pm\ \ldots\ (\textit{0·495})\ \ldots\ \textit{1·760}\ \textit{1·920}\ \ldots$$

This pattern conforms to Type 3 with $i_x = i_y = 3$, and the values of g_x and g_y should be found from

$$g_x = 1{\cdot}920$$
$$g_y = 1{\cdot}760$$

These values expressed in rational numbers are $\frac{2}{1}\frac{3}{2}$ and $\frac{2}{1}\frac{1}{2}$. Again, we have $g_x - g_y = 0{\cdot}495/3 = 0{\cdot}165$, which agrees with those values. Since the values of g are those of the principal and diffuse terms with $i = 3$ in Landé's table it appears that Back has accidentally given the measurement of another Mn I line belonging to the septet system. Assuming that this is the case and that the line is due to the combination $n^7_{23} - n^7_{33}$ the values of g_x and g_y agree exactly with those given by Landé for those terms. This assumption is confirmed by the calculated spacing of the components given by Back, namely,

$$\pm (0{\cdot}167)\ (0{\cdot}334)\ (\textit{0·500})\ 1{\cdot}417\ 1{\cdot}584\ \textit{1·750}\ \textit{1·916}\ 2{\cdot}083\ 2{\cdot}250,$$

whereas the spacing given by $g_x = 2$ and $g_y = \frac{2}{1}\frac{3}{2}$ would be

$$\pm (0{\cdot}083)\ (0{\cdot}167)\ (0{\cdot}250)\ 1{\cdot}750\ 1{\cdot}833\ \textit{1·917}\ \textit{2·000}\ 2{\cdot}083\ 2{\cdot}167.$$

$\lambda = 2605{\cdot}695$. Completely resolved although rather diffuse, the measurements being

$$\pm (0)\ (0{\cdot}347)\ (0{\cdot}694)\ \textit{1·275}\ 1{\cdot}622\ 1{\cdot}969\ 2{\cdot}316\ \ldots$$

This conforms to Type 1 and, there being altogether three p-components, we have $i_x = 3$ and $i_y = 2$. We find therefore that

$$g_x = 1{\cdot}969$$
$$g_y = 2{\cdot}317$$

and in view of the diffuse nature of the Zeeman pattern these are sufficiently near to the rational numbers $\frac{2}{1}$ and $\frac{7}{3}$ which are the values of g calculated by Landé.

It is perfectly clear that this triplet must belong to the septet system from the Zeeman pattern of the first line, $\lambda = 2576{\cdot}116$, from which it was found that in a system of uneven multiplicities one term has $g = 2$ and $i = 3$. This is only possible in a septet system. In view of this the deviations shown by the observations of the third line need cause no anxiety. The values of g are given in Table CLXV.

TABLE CLXV.

i	2	3	4		
g_x		2		n^7_{13}	(sp_i) in the septet system.
g_y	$\frac{7}{3}$	$\frac{23}{12}$	$\frac{7}{4}$	n^7_{2i}	$i = 2, 3, 4$.

Mn^+ multiplet.

λ.	λ.
3497·540	3474·139*
3496·815*	3474·050*
3495·840	3460·332
3488·618	3441·999
3482·918	

The Zeeman effect of the asterisked lines could not be measured owing to overlapping.

$\lambda = 3497{\cdot}540$. Completely resolved, the measurements being

$$\pm (0)\ (0{\cdot}332)\ 1{\cdot}493\ 1{\cdot}825\ \textit{2·157}.$$

This conforms to Type 2, with $i_x = i_y + 1$ and $g_x > g_y$, and consequently $i_x = 2$ and $i_y = 1$. We thus have

$$2g_x - g_y = 2{\cdot}157$$
$$g_x - g_y = 0{\cdot}332,$$

whence

$$\begin{cases} g_x = 1{\cdot}825, & \text{that is } \frac{11}{6} = 1{\cdot}833, \quad \Delta g_x = -0{\cdot}4 \text{ per cent.} \\ g_x = 1{\cdot}493, & \text{that is } \frac{3}{2} = 1{\cdot}500, \quad \Delta g_y = -0{\cdot}5 \text{ per cent.} \end{cases}$$

The calculated positions of the components are

$$\pm (0)\ (0{\cdot}333)\ 1{\cdot}500\ 1{\cdot}833\ \textit{2·166}.$$

$\lambda = 3495{\cdot}840$. This line gives a magnetic triplet of Type 7. From this and the structure of the multiplet we see that $i_y = 0$ and $g_y = 0$ and consequently $i_x = 1$. The measurements were

$$\pm (0)\ 2{\cdot}498,$$

and consequently $g_x = 2{\cdot}498$ or $\frac{5}{2}$.

$\lambda = 3488{\cdot}618$. Completely resolved, the measurements being

$$\pm (0{\cdot}999)\ \ 1{\cdot}499\ \ 2{\cdot}498,$$

which conforms to Type 3. We have therefore

$$\begin{cases} g_x = 2{\cdot}498 \text{ or } \frac{5}{2} \\ g_y = 1{\cdot}499 \text{ or } \frac{3}{2}. \end{cases}$$

the theoretical spacing being

$$\pm (1{\cdot}0)\ \ 1{\cdot}5\ \ 2{\cdot}5.$$

$\lambda = 3482{\cdot}918$. Completely resolved, the measurements being

$$\pm (0{\cdot}3312)\ \ (0{\cdot}6624)\ \ 1{\cdot}165\ \ 1{\cdot}496\ \ 1{\cdot}827\ \ 2{\cdot}158,$$

which again conforms to Type 3. There being two p-components, excluding that one at 0 which is absent, it follows that $i_x = i_y = 2$. We have

$$\begin{cases} g_x = 1{\cdot}827, & \text{that is } \frac{11}{6} = 1{\cdot}833, \quad \Delta g_x = -0{\cdot}3 \text{ per cent.} \\ g_y = 1{\cdot}496, & \text{that is } \frac{3}{2} = 1{\cdot}500, \quad \Delta g_y = -0{\cdot}3 \text{ per cent.}, \end{cases}$$

and hence the calculated spacing of the components is

$$\pm (0{\cdot}333)\ \ (0{\cdot}666)\ \ 1{\cdot}166\ \ 1{\cdot}500\ \ 1{\cdot}833\ \ 2{\cdot}167.$$

$\lambda = 3460{\cdot}332$. Completely resolved, the measurements being

$$\pm (0)\ \ (0{\cdot}329)\ \ (0{\cdot}658)\ \ 0{\cdot}8294\ \ 1{\cdot}159\ \ 1{\cdot}488\ \ 1{\cdot}817\ \ \ldots$$

which conforms to Type 1, with $i_x = 2$ and $i_y = 3$. We have

$$3g_y - 2g_x = 0{\cdot}8294$$
$$2g_y - 2g_x = -0{\cdot}658,$$

whence

$$\begin{cases} g_y = 1{\cdot}4874, & \text{that is } \frac{3}{2} = 1{\cdot}500, \quad \Delta g_y = -0{\cdot}8 \text{ per cent.} \\ g_x = 1{\cdot}8164, & \text{that is } \frac{11}{6} = 1{\cdot}833, \quad \Delta g_x = -0{\cdot}9 \text{ per cent.} \end{cases}$$

The calculated spacing of the components is

$$\pm (0)\ \ (0{\cdot}333)\ \ (0{\cdot}666)\ \ 0{\cdot}833\ \ 1{\cdot}166\ \ 1{\cdot}500\ \ 1{\cdot}833\ \ 2{\cdot}167.$$

$\lambda = 3441{\cdot}999$. Completely resolved as to the p-components, and only partially so as to the s-components on account of distortion. The measurements were

$$\pm (0)\ \ (0{\cdot}1655)\ \ (0{\cdot}331)\ \ (0{\cdot}4965)\ \ 0{\cdot}9992\ \ 1{\cdot}165\ \ 1{\cdot}330\ \ 1{\cdot}496\ \ \ldots$$

This conforms to Type 1 with $i_x = 3$ and $i_y = 4$. Hence we have

$$4g_y - 3g_x = 0{\cdot}9992$$
$$3g_y - 3g_x = -0{\cdot}4965,$$

$$g_y = 1{\cdot}4957, \quad \text{that is } \tfrac{3}{2} = 1{\cdot}500, \quad \Delta g_y = -0{\cdot}3 \text{ per cent.}$$
$$g_x = 1{\cdot}6612, \quad \text{that is } \tfrac{5}{3} = 1{\cdot}667, \quad \Delta g_x = -0{\cdot}4 \text{ per cent.}$$

The calculated spacing of the components is

$\pm$ (*0*) (0·166) (0·332) (0·498) ***1·000*** 1·166 1·333 1·500 1·666 1·833 2·000.

The values of g_x and g_y are assembled in Table CLXVI.

TABLE CLXVI.

i	0	1	2	3	4		
g_x		$\frac{5}{2}$	$\frac{11}{6}$	$\frac{5}{3}$		n^5_{2i}	$i = 1, 2, 3,$
g_y	0	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	n^5_{3i}	$i = 0, 1, 2, 3, 4,$

and as can be seen they agree exactly with the values given by Landé for the p and d terms of the quintet system.

There can be felt but little doubt that these foregoing results of Back give a most remarkable experimental confirmation of Landé's theoretical calculation of the values of his resolution factor. The confirmation of Landé's general theory of the anomalous Zeeman effect must be considered in conjunction with the interval ratios between the lines composing the manganese and iron multiplets, which were discussed in Chapter I. on p. 149 and 188.

One other piece of evidence noted by Back may be mentioned in connection with the line $\lambda = 4472{\cdot}80$ in the Mn^+ spectrum. This line is due to the combination $n^5_{30} - n^5_{41}$, that is to say, $(p_0 d_1)$ in the quintet system. The values of g for these two terms are $\frac{0}{0}$ and 0 respectively, and it is a very remarkable fact that this line shows no Zeeman effect whatever.

Fraülein Gieseler [1] has also verified the Landé values of g from the Zeeman resolution of the arc lines of chromium. As an instance of this we may first take the two principal triplets at

λ.	$\Delta\nu$.	λ.	$\Delta\nu$.
4289·89		3605·48	
	112·43		115·04
4274·96		3593·64	
	81·42		91·49
4254·90		3578·84	

1st Triplet.

$\lambda = 4254{\cdot}90$. The measurements of the components were

$\pm$ (**0**) (1·572) (3·157) **6·278** 7·844 9·358 10·934 12·459.

These values are not expressed in terms of $\Delta\nu_{\text{norm}}$ and therefore must be reduced. There being three p-components which are spaced in the series 0, 1, 2, it is clear that we have a system of uneven multiplicities, and, further, since the first s-component is the most intense, we have $i_x = 3$, $i_y = 2$ and $g_y > g_x$. It follows that

$$3g_x - 2g_y = 6{\cdot}278$$
$$2g_x - 2g_y = -3{\cdot}157.$$

[1] *Ann. der Phys.*, **69**, 147 (1922); *Zeitsch. für Phys.*, **22**, 228 (1924).

whence

$g_x =$ 9·435 or 2·000, that is $\frac{2}{1}$

$g_y =$ 11·013 or 2·335, that is $\frac{7}{3} = 2{\cdot}333$, $\Delta g_y = 0{\cdot}1$ per cent.

The justification for putting $g_x = 2$ is that the triplet is given by the combination (sp_i) and the value of g is 2 for all s terms, except in the singlet system.

In order to reduce the measurements given above to the scale of $\Delta\nu_{\text{norm}}$ they must all be multiplied by 2/9·435. The observed and calculated positions of the components then are

obs. ± (**0**) (0·333) (0·669) **1·331** 1·663 1·984 2·318 2·641.

calc. ± (**0**) (0·333) (0·667) **1·333** 1·667 2·000 2·333 2·667.

Since the s term has $i = 3$ in a system of uneven multiplicities it is evident that the triplet is a principal triplet in the septet system. This is confirmed by the interval ratios between the lines which are

$$81{\cdot}42 : 112{\cdot}43 = \begin{cases} 3{\cdot}0 : 4{\cdot}1 \text{ obs.} \\ 3{\cdot}0 : 4{\cdot}0 \text{ calc.} \end{cases}$$

The value of $\frac{7}{3}$ for g and $i = 2$ is Landé's value and is given very accurately by the above line.

$\lambda = 4274{\cdot}963$. This line was not resolved well but the Zeeman pattern conforms to Type 3. The consideration of the measurements may be postponed until the third line has been dealt with.

$\lambda = 4254{\cdot}503$. Completely resolved into Type 1, the measurements being

± (**0**) (1·174) (2·369) (3·544) **4·702** 5·885 7·058 8·208 9·363 10·524.

It follows that $i_x = 3$, $i_y = 4$ and $g_x > g_y$.
We have therefore

$$4g_y - 3g_x = 4{\cdot}702$$
$$3g_y - 3g_x = -3{\cdot}544,$$

$$\begin{cases} g_y = 8{\cdot}246 \text{ or } 1{\cdot}749, \text{ that is } \frac{7}{4} = 1{\cdot}750 \\ g_x = 9{\cdot}427 \text{ or } 2{\cdot}000. \end{cases}$$

This value of g_y is that given by Landé for the term p_4 in the septet system or n^7_{24}.

The theoretical spacing of the components expressed in terms of $\Delta\nu_{\text{norm}}$ is the series $(g_y - g_x) \times 1, 2, 3$, etc., that is 0·25, 0·5, 0·75, etc. In order to compare the observed measurements, these must be multiplied by 2/9·427.

Obs. ± (**0**) (0·249) (0·503) (0·752) **0·998** 1·249 1·497 1·741 1·987 2·333

Calc. ± (**0**) (0·250) (0·500) (0·750) **1·000** 1·250 1·500 1·750 2·000 2·250 2·500

We may now consider the middle line of the triplet which must be given by the transition $n^7_{13} - n^7_{23}$ and this is confirmed by the absence of the central p-component. Now, Landé's value of g for

the term n^7_{23} is $\frac{2\,3}{1\,2}$ and the question is whether this value can be confirmed. Owing to the bad resolution observed only the two extreme *s*-components, that is the innermost and outermost, could be measured with any accuracy. If the value $\frac{2\,3}{1\,2}$ is correct, then the spacing of the lines should be in terms of $2 - \frac{2\,3}{1\,2} = \frac{1}{1\,2}$. From the combination scheme

m	0	1	2	3
mg_x	0	2	4	6
mg_y	0	$\frac{2\,3}{1\,2}$	$\frac{4\,6}{1\,2}$	$\frac{6\,9}{1\,2}$

the innermost and outermost *s*-components are given by the two arrows and are $\frac{2\,1}{1\,2}$ and $\frac{2\,6}{1\,2}$, respectively. The actual measurements of these two components were

$$\pm 8{\cdot}203 \ldots 9{\cdot}994,$$

and in order to reduce these to the scale of $\Delta\nu_{\text{norm.}}$ they must be multiplied by the same reducing factor as used in the case of the other two lines, namely, 2/9·430 (mean value). The reduced values should be $\frac{2\,1}{1\,2}$ and $\frac{2\,6}{1\,2}$ respectively, and that this is correct can be seen from the following :—

Obs. $\pm 1{\cdot}740 \ldots 2{\cdot}120$
Calc. $\pm 1{\cdot}750 \ldots 2{\cdot}167.$

The agreement is satisfactory in view of the general difficulty of measurement.

2nd Triplet.

This triplet is analogous to the first in every way.

$\lambda = 3605{\cdot}483$. Type 1, with $i_x = 3$ and $i_y = 2$, the measurements being

$$\pm (\mathbf{0})\ (1{\cdot}580)\ (3{\cdot}131)\ \mathbf{6{\cdot}332}\ 7{\cdot}883\ 9{\cdot}423\ 10{\cdot}943\ 12{\cdot}495.$$

It follows that

$$3g_x - 2g_y = 6{\cdot}332$$
$$2g_x - 2g_y = -\,3{\cdot}131,$$

whence $\begin{cases} g_x = 9{\cdot}463 \text{ or } 2 \\ g_y = 11{\cdot}029 \text{ or } 2{\cdot}331, \text{ that is } \frac{7}{3} = 2{\cdot}333. \end{cases}$

From these values of g_x and g_y we obtain the calculated and observed values of the components as follows :—

Obs. $\pm (\mathbf{0})\ (0{\cdot}334)\ (0{\cdot}662)\ \mathbf{1{\cdot}338}\ 1{\cdot}666\ 1{\cdot}992\ 2{\cdot}313\ 2{\cdot}641$
Calc. $\pm (\mathbf{0})\ (0{\cdot}333)\ (0{\cdot}667)\ \mathbf{1{\cdot}323}\ 1{\cdot}667\ 2{\cdot}000\ 2{\cdot}333\ 2{\cdot}667.$

For the same reason as before the middle line may be considered last.

$\lambda = 3578{\cdot}836$. Type I, with $i_x = 3$ and $i_y = 4$, the measurements being

$\pm$ (0) (1·175) (2·350) (3·535) **4·700** 5·885 7·030 8·184 9·329 10·514 11·679.

It follows that

$$4g_y - 3g_x = 4{\cdot}700$$
$$3g_y - 3g_x = -3{\cdot}535,$$

whence $\begin{cases} g_y = 8{\cdot}235 \text{ or } 1{\cdot}750, \text{ that is } \frac{7}{4} \\ g_x = 9{\cdot}413 \text{ or } 2{\cdot}000. \end{cases}$

Reduced to the scale of $\Delta\nu_{\text{norm}}$ the observed and calculated positions of the components are

Obs. $\pm$ (0) (0·250) (0·499) (0·751) **0·999** 1·250 1·494 1·739 1·982 2·234 2·482
Calc. $\pm$ (0) (0·250) (0·500) (0·750) **1·000** 1·250 1·500 1·750 2·000 2·250 2·500

The allocation of this triplet to the septet system is confirmed by the interval ratios, which are

$$91{\cdot}49 : 115{\cdot}04 = \begin{cases} 3{\cdot}0 : 3{\cdot}8 \text{ obs.} \\ 3{\cdot}0 : 4{\cdot}0 \text{ calc.} \end{cases}$$

$\lambda = 3593{\cdot}637$. This line was also incompletely resolved, the innermost and outermost s-components only being measured with any degree of accuracy. For the same reason as given above for the central line of the first triplet these two lines should show separations of $\frac{2}{1}\frac{1}{2}$ and $\frac{2}{1}\frac{6}{2}$, respectively. The measurements were

$$\pm 8{\cdot}279 \ldots 10{\cdot}195.$$

These values must be reduced to the scale of $\Delta\nu_{\text{norm}}$ by multiplication by the ratio 2/9·438 (mean of the values found for the two outer lines of the triplet), and the reduced values compared with the values calculated from $\frac{2}{1}\frac{1}{2}$ and $\frac{2}{1}\frac{6}{2}$ are

Obs. $\pm 1{\cdot}754 \ldots 2{\cdot}160$
Calc. $\pm 1{\cdot}750 \ldots 2{\cdot}167.$

No doubt therefore can be felt as to the correctness of the value $\frac{2}{1}\frac{3}{2}$ for g in the case of the term n^7_{23}. This is very satisfactory since the evidence we obtained previously for this value in the case of manganese was based on an interpretation of the Zeeman pattern given by Back for the Mn I line $\lambda = 2593{\cdot}734$, which is different from that put forward by Back.

As a last example we may take Fraülein Gieseler's measurements of the chromium triplet at

$$\lambda = 5208{\cdot}596$$
$$\lambda = 5206{\cdot}215$$
$$\lambda = 5204{\cdot}692$$

all the lines of which are strongly distorted.

$\lambda = 5208{\cdot}596$. Type 1, the measurements being

$$\pm (\mathbf{0})\ (1{\cdot}537)\ (3{\cdot}100)\ \mathbf{4{\cdot}756}\ 6{\cdot}322\ 7{\cdot}861\ 9{\cdot}109\ ?$$

It is evident that $i_x = 2$, $i_y = 3$, and $g_x > g_y$. We thus have

$$3g_y - 2g_x = 4{\cdot}756$$
$$2g_y - 2g_x = -3{\cdot}100,$$

whence $\begin{cases} g_y = 7{\cdot}856 \text{ or } 1{\cdot}670, & \text{that is } \frac{5}{3} = 1{\cdot}667 \\ g_x = 9{\cdot}406 \text{ or } 2{\cdot}000. \end{cases}$

$\lambda = 5206{\cdot}215$. Type 3, the measurements being

$$\pm \ldots\ (\mathbf{1{\cdot}525})\ 7{\cdot}999\ \mathbf{8{\cdot}989}\ \mathbf{9{\cdot}812}\ \ldots$$

We have $i_x = i_y = 2$ and $g_x > g_y$ and consequently

$$\begin{cases} g_x = 9{\cdot}812 \text{ or } 2{\cdot}000 \\ g_y = 8{\cdot}989 \text{ or } 1{\cdot}832, & \text{that is } \frac{11}{6} = 1{\cdot}833. \end{cases}$$

$\lambda = 5204{\cdot}692$. Type 1, the measurements being

$$\pm (\mathbf{0})\ (2{\cdot}265)\ [8{\cdot}048]\ 9{\cdot}566\ \ldots$$

and $i_x = 2$, $i_y = 1$, and $g_x < g_y$.

In this case the measurement of the strongest s-component is untrustworthy, and the best we can do is to take the second s-component thus

$$g_x = 9{\cdot}566$$
$$g_x - g_y = -2{\cdot}265,$$

whence $\begin{cases} g_y = 11{\cdot}831 \text{ or } 2{\cdot}474, & \text{that is } \frac{5}{2} = 2{\cdot}5 \\ g_x = 9{\cdot}566 \text{ or } 2{\cdot}000. \end{cases}$

The three calculated values of g for the p terms agree well with the values given by Landé, except the last which is 1·3 per cent in error. The distortion of the Zeeman patterns is well shown by the three different ratios 2/9·406, 2/9·812, and 2/9·566. These of course should all be the same, since all three lines were resolved in the same magnetic field and their components measured on the same photographic plate. It is of considerable interest that even in a distorted Zeeman pattern accurate values of g can be obtained. This question of distortion will be discussed in greater detail below, when we come to the question of experimental observation and the methods of measurement.

Up to the present it has been our concern to prove from certain experimental observations that the Landé g-formula is correct, and there can be little doubt that the evidence affords a most striking proof. Although this section is principally devoted to a discussion of Landé's theoretical explanation of the anomalous Zeeman effect, yet it is advisable for the sake of continuity to consider a little more fully the fundamental types, the existence of which has been established by his g-formula. It is hardly necessary to emphasise the fact that

TABLE CLXVII.

$i=$	0	1	2	3	4	5	6	7	1	2	3	4	5	6	7	8	
k																	
1	$\frac{0}{0}$																Singlet system $r=1$
2		1							2								s
3			1						$\frac{2}{3}$	$\frac{4}{3}$							p
4				1						$\frac{4}{5}$	$\frac{6}{5}$						d
5					1							$\frac{6}{7}$	$\frac{8}{7}$				f
						1							$\frac{8}{9}$	$\frac{10}{9}$			g
1		2								2							Triplet system $r=3$
2	$\frac{0}{0}$	$\frac{3}{2}$	$\frac{3}{2}$						$\frac{8}{3}$	$\frac{26}{15}$	$\frac{8}{5}$						s
3		$\frac{1}{2}$	$\frac{7}{6}$	$\frac{4}{3}$					0	$\frac{6}{5}$	$\frac{48}{35}$	$\frac{10}{7}$					p
4			$\frac{2}{3}$	$\frac{13}{12}$	$\frac{5}{4}$					$\frac{2}{5}$	$\frac{36}{35}$	$\frac{78}{63}$	$\frac{4}{3}$				d
5				$\frac{3}{4}$	$\frac{21}{20}$	$\frac{6}{5}$					$\frac{4}{7}$	$\frac{62}{63}$	$\frac{116}{99}$	$\frac{14}{11}$			f
																	g
1			2								2						Quintet system $r=5$
2		$\frac{5}{2}$	$\frac{11}{6}$	$\frac{5}{3}$						12	$\frac{66}{35}$	$\frac{12}{7}$					s
3	$\frac{0}{0}$	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{3}{2}$					5							p
4		0	1	$\frac{5}{4}$	$\frac{27}{20}$	$\frac{7}{5}$			10	28	58	100	14				d
5				1	11	23	19	4	3	15	35	63	9				f
				$\frac{1}{3}$	12	20	15	$\frac{4}{3}$	$-\frac{2}{3}$	16	46	88	$\frac{142}{99}$	$\frac{16}{11}$			g
1				2						15	35	63					Septet system $r=7$
2			$\frac{7}{3}$	23	$\frac{7}{4}$					0	6	8	$\frac{14}{11}$	$\frac{192}{143}$	$\frac{18}{13}$		s
3		3	2	$\frac{7}{4}$	$\frac{33}{20}$	$\frac{8}{5}$					$\frac{7}{6}$	$\frac{7}{7}$					p
4	$\frac{0}{0}$	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{3}{2}$					2					d
5	$-\frac{1}{2}$	$\frac{5}{6}$	$\frac{7}{6}$	$\frac{13}{10}$	$\frac{41}{30}$	$\frac{59}{42}$	$\frac{10}{7}$				$\frac{16}{7}$	$\frac{122}{63}$	$\frac{16}{9}$				Octet system $r=8$
										$\frac{14}{5}$	$\frac{72}{35}$	$\frac{38}{21}$	$\frac{56}{33}$	$\frac{18}{11}$			s
									4	2	$\frac{12}{7}$	$\frac{34}{21}$	$\frac{52}{33}$	$\frac{222}{143}$	$\frac{20}{13}$		p
									$-\frac{4}{3}$	$\frac{14}{15}$	$\frac{44}{35}$	$\frac{86}{63}$	140 99	206 143	284 195	$\frac{22}{15}$	d
																	f
																	g
$i=$	0	1	2	3	4	5	6	7	1	2	3	4	5	6	7	8	
$\Delta\nu=$	1	2	3	4	5	6	7		$=\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$	$\frac{9}{2}$	$\frac{11}{2}$	$\frac{13}{2}$	$\frac{15}{2}$		

so far as the ideal Zeeman pattern of any line is concerned the whole problem may be considered as solved. Provided that the combination is known to which a spectrum line is due, the ideal Zeeman pattern for that line can now at once be written down with the help of Table CLV. on p. 331. As, however, it is more convenient for purposes of calculation to use the conventional values of i, k, and r in place of those of I, K, and R which were given in that table, Table CLXVII. may be given of the values of g referred to the former or conventional quantum numbers.

The words "ideal Zeeman pattern" were used above for the reason that distortion, due to an incipient Paschen-Back effect, is always present to a greater or less degree, though, as will presently be shown, this is not so serious as might at first be expected.

We may now consider the effect on the fundamental types of certain limiting conditions affecting the values of g and i. Some of these are only of academic interest for they have not been observed, but they are none the less interesting. If, for example, in Type I where $i_x = i_y + 1$ and $g_x < g_y$ we were to have the condition that $i_x/g_y = i_y/g_x$ or $i_x g_x = i_y g_y$, then the type would be modified to a scheme such as follows where $i_x = 4$, $g_x = 3$, $i_y = 3$, and $g_y = 4$.

m	0	1	2	3	4
mg_x	0	3	6	9	12
mg_y	0	4	8	12	

which gives as Zeeman pattern

$$\pm (0)\ (1)\ (2)\ (3)\ \mathbf{0}\ 1\ 2\ 3\ 4\ 5\ 6,$$

the first four s-components having the same positions as the p-components.

Again, if in Type I $i_x g_x - i_y g_y$ is less than $g_y - g_x$ as for example

m	0	1	2	3
mg_x	0	5	10	15
mg_y	0	7	14	

the resulting pattern is

$$\pm (0)\ (2)\ (4)\ \mathbf{1}\ 3\ 5\ 7\ 9,$$

in which some of the s-components fall between the p-components. A third case may be added to these, namely, Type I when $i_x g_x - i_y g_y$ is negative, and in this the Zeeman pattern is very interesting. As an example we may take $i_x = 3$, $g_x = 5$, $i_y = 2$, $g_y = 9$

m	-3	-2	-1	0	$+1$	$+2$	$+3$
mg_x	-15	-10	-5	0	5	10	15
mg_y		-18	-9	0	9	18	

$+13\ +9\ +5\ +1\ \mathbf{-3}\ (+8)\ (+4)\ (\mathbf{0})\ (-4)\ (-8)\ \mathbf{+3}\ -1\ -5\ -9\ -13.$

It will be noticed that the strongest s-component has a different sign from the others associated with it and consequently it will be situated on the opposite side of the centre of the pattern. The resulting pattern is shown in Fig. 32, where the two groups of s-components are marked with a circle and cross respectively. At first sight this pattern does not appear in any way to conform to one of the fundamental types and is indeed somewhat surprising. On the other hand, of course, if the s-components are grouped together in the way indicated the structure becomes quite simple to understand.

Similar variations in the types 2 — 6 may be studied by setting limiting conditions to the values of g_x and g_y. The alternation of

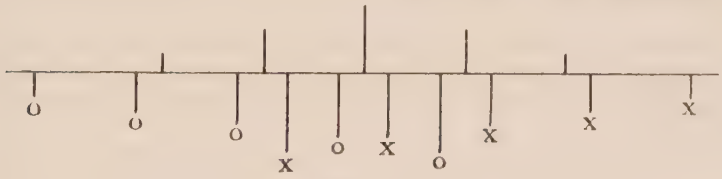


FIG. 32.

p- and s-components in Types 4 and 6 has already been instanced in the case of the multiplets in the arc spectrum of manganese.

A particularly interesting case is afforded by the combination $n^4_{32} - n^4_{42}$ which should give Type 6, since $i_x = i_y = 2$ in the quartet system. The peculiarity of the resulting pattern is caused by the fact that $g_x = \frac{6}{5}$ and $g_y = \frac{2}{5}$, that is to say, $g_x = 3g_y$. The scheme of combination is as follows :—

m	$-\frac{3}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{3}{2}$
mg_x	$-\frac{9}{5}$	$-\frac{3}{5}$	$+\frac{3}{5}$	$+\frac{9}{5}$
mg_y	$-\frac{3}{5}$	$-\frac{1}{5}$	$+\frac{1}{5}$	$+\frac{3}{5}$

$\pm(2)\ (\mathbf{6})\ 0\ \mathbf{4}\ 8$

5

and at first sight this appears to be perfectly normal. It must be noted, however, that there are two s-components, one at $+0$ and the other at -0. These two, therefore, coincide with the result that the

intensity of the apparently single component at 0 has a greater intensity than the ones at $\pm \frac{4}{5}$, the actual intensity being $\frac{2}{3} + \frac{2}{3} = \frac{4}{3}$, that of the components at ± 4 being 1. The observed intensities of the components would be as in Fig. 33,

Fig. 33.

$$i.e. \quad \frac{\pm (2)\ (6)\ 0\ 4\ 8}{5},$$

which does not conform to any type. Recognition of the fact that the *s*-component at 0 is made up of two components shows that the observed intensity must be reduced to one-half, when of course the pattern conforms to Type 6. As Back points out this has been observed in the case of the line $\lambda = 3128{\cdot}82$ in the Cr^+ spectrum, which is due to the combination $n^4_{32} - n^4_{42}$.

There remain to be mentioned the so-called pseudo-types, to which reference has already been made. These pseudo-types are obtained when g_x is very nearly the same as g_y, so that the difference between them, that is the difference between consecutive components, is very small. The components then cannot be resolved in the photograph of the Zeeman pattern. We have already come across two instances, namely, a pseudo-quartet given by $\lambda = 3790{\cdot}215$ and a pseudo-triplet given by $\lambda = 3806{\cdot}866$, both lines being part of the multiplet at $\lambda = 3777$ to $\lambda = 3844$ in the arc spectrum of manganese. The Zeeman patterns for both lines may be calculated in order that we may see how, in spite of the practical impossibility of resolution, the type may be recognised. $\lambda = 3790{\cdot}215$, $i_x = i_y = 5$, $g_x = \frac{14}{9} = \frac{154}{99}$, $g_y = \frac{142}{99}$, sextet system.

m	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$	$\frac{9}{2}$
mg_x	-77	77	231	385	539	693
mg_y	-71	71	213	355	497	639

$\pm$ (6) (18) (30) (42) (**54**) 100 112 124 136 **148** 160 172 184 196

99

The distance between any two consecutive components of the same type is therefore $\frac{12}{99}$, or a little less than $\frac{1}{8}$th of the normal triplet interval. The failure to resolve the components would lead to a pattern such as in Fig. 34, hence the name pseudo-quartet.

Fig. 34.

$\lambda = 3806{\cdot}866$. $i_x = 5$, $i_y = 6$, $g_x = \frac{14}{9} = \frac{154}{99}$, $g_y = \frac{16}{11} = \frac{144}{99}$, sextet system.

m	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$	$\frac{9}{2}$	$\frac{11}{2}$
mg_x	-77	77	231	385	539	693	
mg_y	-72	72	216	360	504	648	792

$\pm$ (5) (15) (25) (35) (45) 99 109 119 129 139 149 159 169 179 189 99

Here the distance between any two consecutive components is $\frac{10}{99}$ or about $\frac{1}{10}$th of the normal triplet interval. The unresolved Zeeman pattern would appear as in Fig. 35, hence the name pseudo-triplet. This type of pseudo-triplet is given by the fundamental types 1 and 4, whereas the fundamental types 2 and 5 give the type of pseudo-triplet shown in Fig. 36. It may be seen from the last three figures that the recognition of the fundamental type to which a given Zeeman pattern belongs presents little difficulty, even if the distance

Fig. 35.

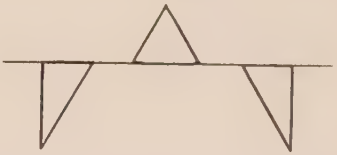


Fig. 36.

between the consecutive components is too small to permit of their resolution. If the position of the maxima can be determined in these pseudo-types, then it is possible to arrive at an accurate allocation of the line to its series and system if Landé's values of g be taken as correct.

In concluding this section dealing with the theory of the anomalous Zeeman effect it is impossible to omit an expression of our indebtedness to Dr. Back for his work in experimentally verifying the Landé g values, since the combination of theorist and experimenter in the University of Tübingen has given us what may be looked upon as a full and complete solution of the anomalous Zeeman phenomenon. Yet these two would be, and indeed are, the first to recognise the remarkable foundation built by that great philosopher Sommerfeld, who, by his concept of inner quantum numbers, made the first step in the advance, which has now been consolidated.

The Paschen-Back Effect. This phenomenon, which was discovered in 1912 by Paschen and Back,[1] is one of very great interest and importance. In spite of the fact that this work was carried out

[1] *Ann. der Phys.*, **39**, 897 (1912); **40**, 960 (1913).

eight years before the first explanation of the anomalous Zeeman effect on the quantum theory was enunciated by Sommerfeld, it is more convenient to discuss it at this stage, because the phenomenon and its explanation play an integral and essential part in the complete elucidation of the Zeeman effect.

Brief references have already been made to the disturbance in the symmetry of an anomalous Zeeman pattern due to the effect of neighbouring lines, the magnitude of this distortion depending on the strength of the outer magnetic field and also on the proximity of the spectral lines. Paschen and Back dealt with this phenomenon, and they succeeded in showing that this distortion increases with increase in the outer magnetic field until finally when the field is sufficiently strong the Zeeman pattern originally anomalous becomes a true normal triplet. In describing their investigations we may follow their line of argument from the beginning, bearing in mind of course that at that time the Bohr theory with all its subsequent developments as to multiplets had not been conceived. To Paschen and Back the most complex line structure known was the diffuse triplet with its six lines, and so perhaps their ideas may now seem somewhat archaic.

They start from the position that relatively few spectrum lines exhibit the normal Zeeman triplet, such for instance as

$\lambda = 6362{\cdot}345$	Zn	diffuse series
6438·47	Cd	,, ,,
4916·18 }	Hg	sharp series
4108·17 }		
4347·62	Hg	diffuse series
5528·47 }	Mg	,, ,,
4703·07 }		
2288·79	Cd	principal series
4226·73	Ca	,, ,,
2852·13	Mg	,, ,,

and that these lines stand out in comparison with the very varied anomalous types exhibited by other lines. In general, Preston's law holds good as regards the anomalous effect, namely, that all the lines of one spectral series exhibit the same Zeeman type with the same separation in the same field, and that the corresponding lines of different elements are characterised by the same Zeeman pattern.

Again, the anomalous Zeeman effect is only exhibited by those lines for which at least one of the series terms bears an index number, and the magnetic type of that combination is fixed and is independent of the element and the order number of the combination. In other words, lines of a singlet system never show an anomalous Zeeman effect, whilst doublets and triplets expressed by $p_i - md_i$, $p_i - m\mathrm{S}$, etc., always do so. So far as the anomalous Zeeman effects had been observed, they fell in with this scheme with very few exceptions,

which were due partly to experimental errors and partly to the phenomenon now to be described.

When, however, we come to look into the question in detail, we find that the above general scheme only holds good if the complete structure of a doublet or triplet is developed. For example, if the three satellites of a diffuse triplet lie so close to the principal lines that they cannot be separated, with the result that the triplet consists of only three lines in place of the normal six lines, then the magnetic resolution of the three lines is less complex than that of the six lines of a fully developed triplet.

Similarly, if the satellites lie very close to the principal lines but still clearly visible, the general scheme does not hold good, that is to say, the Zeeman pattern differs from that characteristic of a diffuse triplet.

An excellent example of this is afforded by the magnesium line $\lambda = 3838$, which is the first principal line of the first diffuse triplet. This line should have two satellites such as are shown by the corresponding lines of mercury ($\lambda = 3650$, 3655, and 3663) and cadmium ($\lambda = 3611$, 3613, and 3615), but they cannot be seen separated from the principal line. We should expect in the case of this line, when examined in a magnetic field, a superposition of the three anomalous patterns given alike by the three mercury and the three cadmium lines. In place of that a much simpler Zeeman type is found, which, as a matter of fact, is the same as that given by the first line of a sharp triplet of mercury, *e.g.* $\lambda = 5461$.

A still more remarkable instance is afforded by the principal series of lithium ($\lambda = 6707{\cdot}8$, 3282·8, 2741·4, etc.), the lines of which (by analogy with the other alkali metals) must consist of very narrow doublets. We would expect these lines to give Zeeman patterns consisting of the superimposed types of D_2 and D_1. These lines, however, exhibit a true normal triplet. Similarly the two lines of the diffuse series of lithium ($\lambda = 6103{\cdot}5$ and 4603·1) should give as Zeeman pattern the superimposed types of the three lines of a normal diffuse doublet. These lines again give the normal triplet.

It is evident from these last two instances that the normal triplet is given not only by a truly single line, but also by a very narrow doublet or triplet. If a narrow doublet, such for example as $\lambda = 6708$ of lithium, were resolved by means of a spectroscope of sufficiently high resolving power, it would be expected that in a very weak magnetic field the two components would give the D_2 and D_1 Zeeman types respectively. If the final result is that in a strong magnetic field the normal triplet is obtained, there lies here a new phenomenon as regards the effect of a magnetic field on spectrum lines. The magnetic field must be able to destroy a series doublet and produce therefrom a single line.

Paschen and Back investigated some very narrow, but clearly resolved, doublets and triplets in order to put this deduction to the test of experiment, the effect of small and large fields being tried.

The narrowest triplet known to them was that of oxygen at $\lambda = 3947$ which, as shown by Runge and Paschen,[1] is the second member of the principal series of triplets $1s - 3p_i$. The three lines should show the following Zeeman patterns :—

		λ.	Magnetic Types.
Strongest line .	$1s - 3p_1$	3947·438	5461 Hg, 5183 Mg, 5086 Cd, etc.
Middle ,, .	$1s - 3p_2$	3947·626	4358 Hg, 5173 Mg, 4800 Cd, etc.
Weakest ,, .	$1s - 3p_3$	3947·731	4047 Hg, 5168 Mg, 4678 Cd, etc.

Indeed, in magnetic fields smaller than 6000 Gauss each of the three lines is separately resolved, as can clearly be seen by their broadening. With slowly increasing magnetic field, the change in the Zeeman phenomenon commences as soon as the magnetically resolved components interfere with one another, and particularly as soon as the outside components of one line fall on the middle of the next line. When the field strength reaches 11,000 Gauss none of the components of the original lines can be recognised. Those which are still visible do not lie in their calculated positions and they become weaker as the field is still further increased.

A strong middle component makes its appearance at $\lambda = 3947{\cdot}564$, which is very nearly the optical centre of gravity of the original triplet. In the weaker fields this component is incompletely polarised, but with a field of 32,000 Gauss it appears as a completely polarised *p*-component. The two *s*-components appear separated at 20,000 Gauss, but they are very broad and hazy. They are almost completely polarised, the exact amount of polarisation being difficult to determine on account of the small intensity. At 32,000 Gauss these *s*-components appear quite separated from the middle *p*-component and are less broad. With still stronger fields the central component appears as a sharp line, whilst the two outer *s*-components are broad with sharply defined edges so that they definitely appear as broadened lines. Since the edges of the latter could be accurately measured, it was possible to take the mean values of the wave-lengths of the edges of each side component and thereby obtain an accurate value of the triplet separation. This separation in a field of 34,860 Gauss was found, as the mean of three sets of measurements, to be $\Delta\lambda = 0{\cdot}510$, the true value for the normal triplet being $\Delta\lambda = 0{\cdot}511$. In a field of 39,927 Gauss the mean of nine sets of measurements gave $\Delta\lambda = 0{\cdot}573$, the true value for the normal triplet being $\Delta\lambda = 0{\cdot}584$.

The wave-lengths of the central *p*-component determined at different strengths of the magnetic field were as follows :—

H	12774	21829	31899	34860	39927
λ	3947·610	3947·572	3947·554	3947·544	3947·541

The final position of the central component is almost identical with the optical centre of gravity of the original triplet. Paschen and

[1] *Ann. der Phys.*, **61**, 641 (1897).

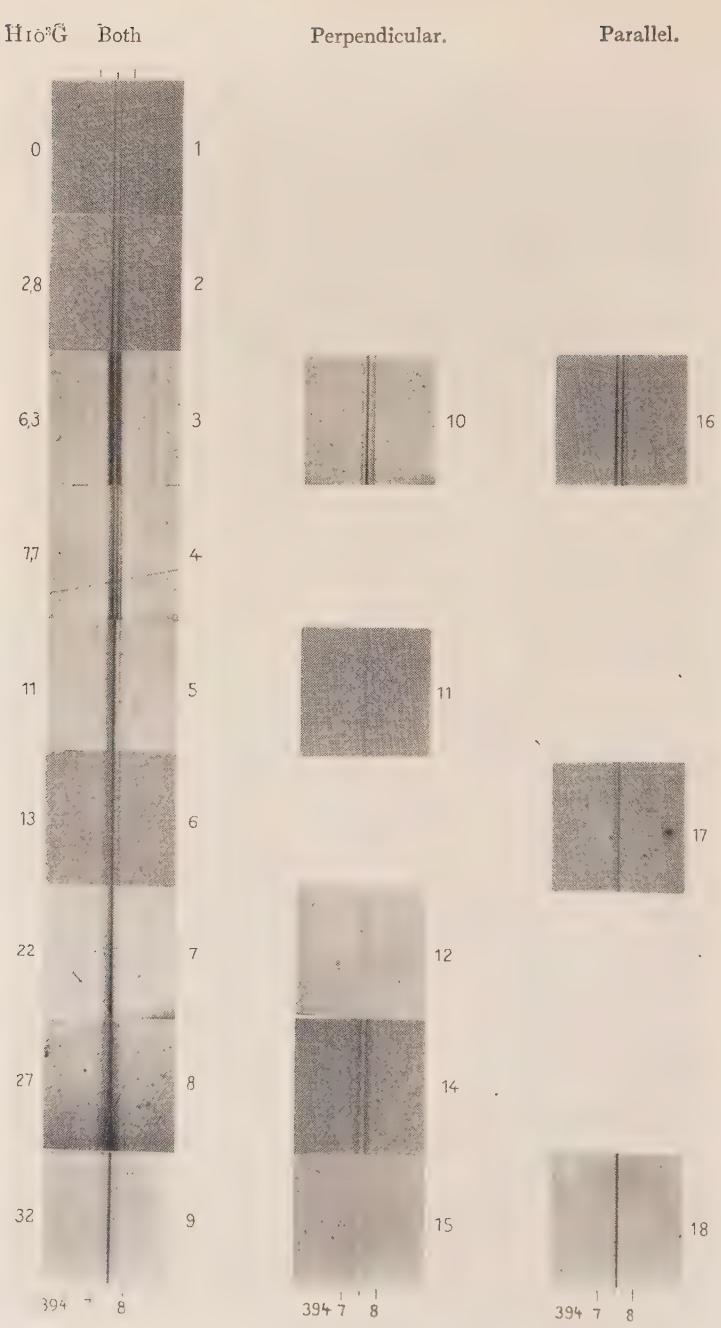


FIG. 37.

(*From "Annalen der Physik,"* **39**, 897 (1912), *Paschen and Back.*)

[*To face page* 375.

Back give this as 3947·556 on the assumption that the intensities of the three lines are 10, 7, and 4. We now know, however, by the work of Burger and Dorgelo that the intensities are proportional to the inner quantum numbers of Landé, *i.e.* $\frac{5}{2}$, $\frac{3}{2}$, and $\frac{1}{2}$ or 5, 3, and 1. The true optical centre of gravity of the triplet is therefore 3947·5332 which clearly has practically been reached at 40,000 Gauss.

The breadth of the central *p*-component was found to be 0·086 A. or, in wave-numbers, 0·55 cm.$^{-1}$. The latter value is the same as that of the normal triplet given in the same magnetic field by the oxygen line $\lambda = 4368$. This line, which is the second member of the principal series of doublets and therefore must be a very narrow pair like the lithium lines, gives an exact normal triplet in all strengths of magnetic field.

In conclusion Paschen and Back say : " The remarkable definition of the central *p*-component and the exact normal resolution exhibited by the centres of the two *s*-components show that so close an approximation is reached to the normal Zeeman triplet, that we are correct in viewing, on the observed facts only, the normal triplet as the final stage of the changes produced by increasing the magnetic field."

The various stages in the development of the normal Zeeman triplet with increasing magnetic field are shown in Fig. 37, 1 to 9. The perpendicular components are shown in 10 to 15, and the parallel components in 16 to 18. These very interesting photographs are reproduced with Professor Paschen's permission from the paper published by him with Dr. Back. The following detailed observations may be given :—

	Gauss.	
1	0	The original oxygen triplet.
2	2800	The three lines are broadened.
3	6187	The lines are more broadened, but are still separated.
4	7738	The right-hand edge of the line on the left is strengthened.
5	10930	The central *p*-component has now appeared for the first time.
6	12770	New components make their appearance and in particular there is a diffuse and broad portion on each side.
7	21830	
8	27880	
9	31900	The new components have disappeared ; the central *p*-component is now fully developed, whilst the two *s*-components are still in process of development and appear very broad and faint, but quite separate from the central component.
10-15		Perpendicular components only, the strengths of the field being 6500, 11260, 19770, 27720, and 32430 Gauss, respectively.
16	6500	The parallel components of the three lines ; compare 3 and 10.

	Gauss.	
17	12000	This was taken in the second order of the grating, all the others being in the third order, parallel components only.
18	32000	The middle p-component is completely polarised and is the only one present.

The Theory of the Paschen-Back Effect.—The first explanation of the Paschen-Back effect on the basis of the quantum theory was given by Sommerfeld. It is very evident from the experimental facts noted in the preceding section that in stating the Paschen-Back effect in the form "all spectrum lines when examined in a strong magnetic field exhibit the normal triplet," some explanation of the meaning of the word "strong" is required. Thus we learn that the narrow lithium doublets give the normal triplet in any strength of field, we learn that a field of 40,000 Gauss is required to obtain the normal triplet from the oxygen triplet at $\lambda = 3647$, and we know that the anomalous Zeeman patterns of the D lines can be studied with but little evidence of distortion being found therein. It is obvious indeed that the strength of a magnetic field is in reality a relative term, relative to the separation between the component lines of doublet, triplet, or multiplet as the case may be. A strong field is one for which the normal triplet separation $\Delta\nu_{\text{norm}}$ is large compared with the separation $\Delta\nu$ between the component lines of the spectral term under investigation. A weak field is one for which $\Delta\nu_{\text{norm}}$ is small compared with the separation $\Delta\nu$ between the consecutive lines of the spectral term.

Let us consider a diffuse series $(p_i d_i)$ in which the difference between the d terms is very small compared with that between the p terms. It will clearly be possible in such a case to imagine a magnetic field which is strong in relation to the d terms and weak in relation to the p terms. In this case the d terms would behave as a single term and the resulting Zeeman pattern of the series lines would not be the normal triplet given by a singlet line, nor would it be the anomalous type characteristic of the diffuse series, but it would be something in between the two or what is known as the partial Paschen-Back effect.

It must be definitely understood that the Paschen-Back effect only concerns spectrum lines which are connected together by series relationships. Two lines which have no series relationships exhibit no evidence of the effect, however closely they may be situated in the spectrum or however much their Zeeman patterns overlap one another.

In 1913 Voigt[1] brought forward an explanation of the Paschen-Back effect for the D_2 and D_1 lines based, like the theory of Lorentz for the normal triplet, on the classical theory. A formal simplification of this theory was published by Sommerfeld,[2] who some years

[1] Waldemar Voigt, *Ann. der Phys.*, **41**, 403; **42**, 210 (1913).
[2] *Göttinger Nachr.*, March, 1914.

later, as the result of his expression of the magnetic resolution as the difference between the magnetic resolution of the combining terms, made use of a similar analysis with respect to the displacements predicted by the Voigt theory for the components of the Zeeman pattern. In this way Sommerfeld was able to express the Voigt theory in terms of the quantum theory.[1]

He starts from Voigt's equations of vibration and calculates the vibration numbers in terms of the ratio

$$v = \frac{\Delta\nu_0}{\Delta\nu_{\text{norm}}} = \frac{H_i}{H}, \quad . \quad . \quad . \quad . \quad (50)$$

where $\Delta\nu_0$ is the wave-number difference between the two D lines. $\Delta\nu_{\text{norm}}$ is proportional to the outer field strength H, and as H_i is the inner magnetic field to which the double nature of the p term is due $\Delta\nu_0$ is proportional to H_i. It follows that v is inversely proportional to the strength of the external magnetic field, being large for "weak" fields and very small for "strong" fields.

Now, the D lines are due to the combination $1\sigma - 2\pi_2$ (D_2 line) and $1\sigma - 2\pi_1$ (D_1 line)[2] and we know that the σ term is single and gives magnetic levels with normal separations, and consequently by subtraction of the $\Delta\nu_{\text{norm}}$ of the σ term from Voigt's values of $\Delta\nu$ for the components Sommerfeld obtained the magnetic resolutions of the two π terms for the various magnetic or equatorial quantum numbers which function in the D lines. At that time Sommerfeld used for the magnetic quantum in the case of doublet systems the values $m = \pm 1$ and ± 3, and he arrived at the following expression for the energy of the various π levels expressed in terms of $\Delta\nu_{\text{norm}}$:—

$$W = W_m + \frac{h}{2}(m \pm \sqrt{1 + \tfrac{2}{3}mv + v^2}) \quad . \quad . \quad (51)$$

where W_m is the energy of the mean position between the two D lines, 3 is the Runge denominator for the π terms, the upper sign refers to the π_2 levels and the lower sign refers to the π_1 levels.

In order to make this formula general for all the terms of a doublet system it is only necessary to replace the value 3 by $2k - 1$, which, as was shown previously, is the general value of the Runge denominator for doublet terms. We then have for the energy

$$W = W_m + \frac{h}{2}\left(m \pm \sqrt{1 + \frac{2mv}{2k-1} + v^2}\right) \quad . \quad . \quad (52)$$

and for the separation in wave-numbers between the levels

$$\Delta\nu = \tfrac{1}{2}\left(m \pm \sqrt{1 + \frac{2mv}{2k-1} + v^2}\right) \quad . \quad . \quad (53)$$

[1] *Zeitsch. für Phys.*, **8**, 257 (1922).

[2] The index numbers adopted are based on the inner quantum numbers.

It must be noted that $\Delta\nu$ is expressed in terms of $\Delta\nu_{\text{norm}}$ and is measured from the mean position between the two doublet terms. Since at the present time the values of m used for doublet systems are $\pm\frac{1}{2}$, $\pm\frac{3}{2}$, (53) is to be written in the form [1]

$$\Delta\nu = m \pm \tfrac{1}{2}\sqrt{1 + \frac{2mv}{k-\frac{1}{2}} + v^2} \quad . \quad . \quad (53a)$$

We may now consider (53a) and its meaning when v is very large and when v is vanishingly small. In the first place, when v is much greater than unity (weak fields),

$$\sqrt{1 + \frac{2mv}{k-\frac{1}{2}} + v^2} = v\left(1 + \frac{m}{k-\frac{1}{2}}\cdot\frac{1}{v} + \ldots\right),$$

and consequently to a first approximation we may put

$$\tfrac{1}{2}\sqrt{1 + \frac{2mv}{k-\frac{1}{2}} + v^2} = \frac{v}{2} + \frac{m}{2k-1} = \frac{\Delta\nu_0}{2} + \frac{m}{2k-1},$$

since from (50) we may put $v = \Delta\nu_0$, the whole expression being in terms of $\Delta\nu_{\text{norm}}$. It follows from this that in the case of weak fields (53a) can be written to a first approximation

$$\Delta\nu \mp \frac{\Delta\nu_0}{2} = m\left(1 \pm \frac{1}{2k-1}\right) \quad . \quad . \quad . \quad (54)$$

It will be remembered that $\Delta\nu$ is measured from the mean position between the two doublet terms and consequently the left-hand side with its upper and lower sign stands for the magnetic resolution of the doublet term with larger and smaller inner quantum number, respectively. We have already seen that the magnetic resolution of any term is given by mg and, therefore, from (54) we should have for all doublet terms

$$g = 1 \pm \frac{1}{2k-1} \quad . \quad . \quad . \quad . \quad (55)$$

the upper and lower sign again being applicable to the terms with larger and smaller inner quantum number, respectively. If in (55) we put $k = 2$, 3, 4, and 5 for the π, δ, etc., terms we obtain at once the values of g given in Table CLXVII. on p. 367. This at once supplies a proof of the validity of Sommerfeld's formula (53a) since it explains the anomalous Zeeman effect as obtained in weak fields when v is very large.

If now for the limiting case of a strong field we put $v = 0$, then (53a) becomes at once

$$\Delta\nu = m \pm \tfrac{1}{2} \quad . \quad . \quad . \quad . \quad (56)$$

[1] Sommerfeld, *Atombau und Spektrallinien*, 4th Auflage, p. 672.

and as $m = \pm\frac{1}{2}, \pm\frac{3}{2}$, etc., the magnetic resolution now becomes an integral multiple of $\Delta\nu_{\text{norm}}$. In other words, the magnetic levels of any term are no longer separated by the amount g but by $\Delta\nu_{\text{norm}}$. It is very interesting to follow the changes in the values of the magnetic levels of the various terms as the magnetic field changes from weak to very strong. These are shown in Table CLXVIII., and it must be noted that those levels which were normal in the case of weak fields remain normal in strong fields. For example, the two normal levels of the σ term remain unchanged on passing from weak to strong fields.

TABLE CLXVIII.

m.	π_2.		π_1.		δ_3.		δ_2.		ϕ_4.		ϕ_3.	
	w.	s.	w.	s.	w.	s.	w.	s.	w.	s.	w.	s.
$+\frac{7}{2}$									$4 \to 4$			
$+\frac{5}{2}$					$3 \to 3$				$\frac{20}{7} \to 3$		$\frac{15}{7} \to 2$	
$+\frac{3}{2}$	$2 \to 2$				$\frac{9}{5} \to 2$		$\frac{6}{5} \to 1$		$\frac{12}{7} \to 2$		$\frac{9}{7} \to 1$	
$+\frac{1}{2}$	$\frac{2}{3} \to 1$		$\frac{1}{3} \to 0$		$\frac{3}{5} \to 1$		$\frac{2}{5} \to 0$		$\frac{4}{7} \to 1$		$\frac{3}{7} \to 0$	
$-\frac{1}{2}$	$-\frac{2}{3} \to 0$		$-\frac{1}{3} \to -1$		$-\frac{3}{5} \to 0$		$-\frac{2}{5} \to -1$		$-\frac{4}{7} \to 0$		$-\frac{3}{7} \to -1$	
$-\frac{3}{2}$	$-2 \to -2$				$-\frac{9}{5} \to -1$		$-\frac{6}{5} \to -2$		$-\frac{12}{7} \to -1$		$-\frac{9}{7} \to -2$	
$-\frac{5}{2}$					$-3 \to -3$				$-\frac{20}{7} \to -2$		$-\frac{15}{7} \to -3$	
$-\frac{7}{2}$									$-4 \to -4$			

Since all the terms are magnetically resolved in a strong field into normal levels, it follows that when a line given by a combination of two of these terms is resolved in a strong field, the components must be separated by the normal interval. Some of the components will be found from the scheme of combination of the magnetic levels to have intervals of $\Delta\nu_{\text{norm}} \times 2$, 3, etc., but these have vanishingly small intensity. This is to be explained by an extension of the selection principle which will be discussed below.

Now up to the present we have considered $\Delta\nu$ of the magnetic levels of the various doublet terms as being measured from the mean position of the terms. We know, however, from the Paschen-Back results that the central p-component of the normal triplet occupies the optical centre of gravity of the doublet, or Voigt's "Schwerpunkt,"

and we have to find an explanation of this. Sommerfeld [1] determines the position of the central line of the Paschen-Back normal triplet in the following way. The value of $\Delta\nu$ given in (56) was obtained by putting $v = 0$, but this must be substituted, in the case of the approximation of v to 0, by

$$\left.\begin{aligned}\Delta\nu &= m \pm \tfrac{1}{2}\left(1 + \frac{mv}{k - \tfrac{1}{2}}\right)\\ &= m \pm \tfrac{1}{2} \pm \frac{mv}{2k - 1}\end{aligned}\right\} \quad . \quad . \quad . \quad (57)$$

If we put $\Delta\nu = \dfrac{\Delta\nu'}{\Delta\nu_{\text{norm}}}$ where $\Delta\nu'$ is the required position measured in wave-numbers from the mean position, then from (57) we have

$$\frac{\Delta\nu'}{\Delta\nu_{\text{norm}}} = m \pm \tfrac{1}{2} \pm \frac{m\dfrac{\Delta\nu_0}{\Delta\nu_{\text{norm}}}}{2k - 1}$$

and

$$\Delta\nu' \mp \frac{m}{2k - 1}\,\Delta\nu_0 = (m \pm 1)\Delta\nu_{\text{norm}} \quad . \quad . \quad (58)$$

In order to find the position of the central or p-component of the Paschen-Back normal triplet we must put $m \pm \tfrac{1}{2} = 0$, that is to say, $m = \mp \tfrac{1}{2}$, where the upper and lower signs still refer to the terms with larger and smaller inner quantum numbers, respectively. Inserting these values of m in the left-hand side of (58) we obtain for both the terms

$$\Delta\nu' + \tfrac{1}{2}\frac{\Delta\nu_0}{2k - 1} = 0 \quad . \quad . \quad . \quad . \quad (59)$$

Applying this to the π terms for which $k = 2$ we find

$$\Delta\nu' + \frac{\Delta\nu_0}{6} = 0,$$

that is to say, the central p-component is situated at a position which is distant from the mean position on the short wave side by $\frac{1}{6}$th of the interval between the two terms. This as a matter of fact is the position of the optical centre of gravity in the case of the D lines since the intensities are $D_2 : D_1$ as 2 : 1 and consequently the optical centre of gravity is distant from D_2 by $\frac{1}{3}$rd of the interval between D_2 and D_1.

Sommerfeld gives in his paper a diagram representing the change from the anomalous Zeeman pattern given by the D lines in weak fields to the Paschen-Back normal triplet theoretically given in strong fields. I say theoretically because the field strength necessary to give the normal triplet would be about 180,000 Gauss which is beyond practical limits at the present time. This diagram is reproduced in Fig. 38. The upper part of the diagram gives the two

[1] *Loc. cit.*, p. 676.

D lines (the term symbols π_1 and π_2 are the old spectroscopic convention) with their anomalous Zeeman components as obtained in weak fields, the polarisation being denoted by the Greek letters σ and π as is common in German literature. At the lower part of the diagram is given the normal triplet of the Paschen-Back effect as would be obtained with fields of, say, 200,000 Gauss. The straight lines indicate the positions to which each anomalous component wanders with the change in field, but it must not be imagined that in fields of intermediate strengths the components would be given by these straight lines.

The two outermost *s*-components have zero intensity, as also have those *p*-components which coincide with the real *s*-components

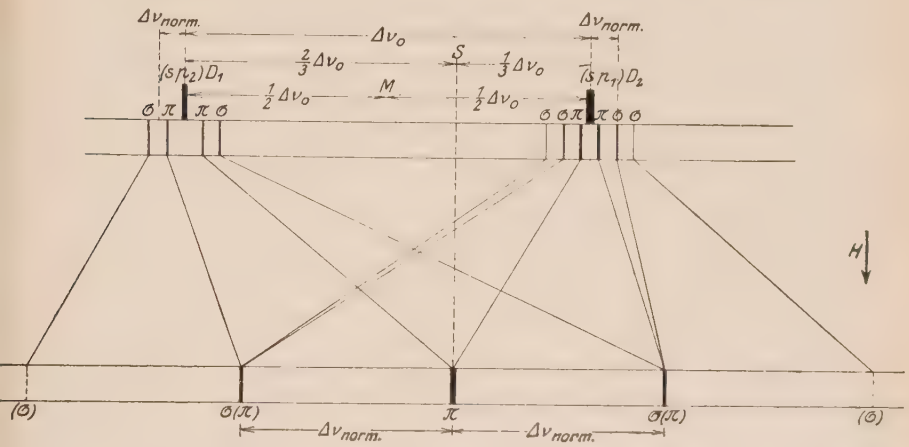


FIG. 38.

(*From "Zeitschrift für Physik,"* **8**, 1, *p.* 259.)

of the normal triplet. This is due to the extension of the selection principle to which we shall come presently.

Landé expresses the Sommerfeld equation (53*a*) in a different form which is more convenient for a subsequent generalisation to systems more complex than the doublet system.[1] He expresses the magnetic resolution of the terms with reference to the optical centre of gravity ν_c of the doublet. He writes (53*a*) in the form

$$\Delta\nu = \nu_c + o m - \frac{\omega}{4K} \pm \sqrt{o^2 + \frac{2m}{K} o\omega + \omega^2} \quad . \quad (60)$$

where o is the normal triplet interval, ω is the separation of the doublet terms, and K is his value for the azimuthal quantum number

[1] *Zeitsch. für Phys.*, **19**, 112 (1923).

($K = k - \frac{1}{2}$ in Sommerfeld's notation, see p. 146). For weak fields when ω is much greater than o, (60) becomes

$$\left.\begin{aligned} \Delta\nu &= \nu_c + \omega\left(\pm\tfrac{1}{2} - \frac{1}{4K}\right) + om\left(1 \pm \frac{1}{2K}\right) \\ &= \nu_c + \omega\gamma + omg \end{aligned}\right\} \quad . \quad (61)$$

As we are dealing with weak fields it is obvious that $\nu_c + \omega\gamma = 0$, since we know that in the anomalous Zeeman effect $\Delta\nu = omg$.[1] This gives at once an opportunity of testing the validity of (61) for the π_1 and π_2 terms where $\nu_c = \pi_2 - \omega/3 = \pi_1 + 2\omega/3$. It follows that for π_2 $\gamma = \frac{1}{3}$ and for π_1 $\gamma = -\frac{2}{3}$, and since K for the principal terms $= \frac{3}{2}$, these are the values of $\pm\frac{1}{2} - \frac{1}{4}K$. This proof, of course, is similar to that by Sommerfeld given previously.

For strong fields, when o is much greater than ω, we have from (60) to a first approximation

$$\left.\begin{aligned} \Delta\nu &= \nu_c + \omega\left(\pm\frac{m}{2K} - \frac{1}{4K}\right) + om\left(1 \pm \frac{1}{2m}\right) \\ &= \nu_c + \omega\gamma + omg \end{aligned}\right\} \quad . \quad (62)$$

In order to differentiate between the γ and g in (61) and (62) we may write for weak fields

$$\Delta\nu = \nu_c + \omega\gamma_w + omg_w,$$

$$\text{where} \quad \gamma_w = \pm\tfrac{1}{2} - \frac{1}{4K}, \quad \text{and} \quad g_w = 1 \pm \frac{1}{2K},$$

and for strong fields

$$\Delta\nu = \nu_c + \omega\gamma_s + omg_s,$$

$$\text{where} \quad \gamma_s = \pm\frac{m}{2K} - \frac{1}{4K}, \quad \text{and} \quad g_s = 1 \pm \frac{1}{2m}.$$

Reference was made above to the recognition by Heisenberg of the constant average value of g for various terms having the same azimuthal quantum numbers, this average value being 1 when the permanent multiplicity is reached and 2 before that stage in any system. He also showed that in a doublet system the sum of the values of mg_w is equal to the sum of the values of mg_s for any pair of terms having the same k and m but different I.[2] This can be seen at once from Table CLXIX. which gives the values of $mg_w \rightarrow mg_s$ for the two ϕ terms.

This permanence of the sums of the values of mg in passing from weak to strong fields was shown by Pauli[3] to hold good for all systems of multiplicities. Expressed in his own words: The sum of the energy values in all those stationary states which appertain to given values

[1] See equation (29) on p. 329. [2] *Zeitsch. für Phys.*, **8**, 273 (1922).
[3] *Ibid.*, **16**, 155 (1923).

TABLE CLXIX.

m	$-\frac{7}{2}$	$-\frac{5}{2}$	$-\frac{3}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{3}{2}$	$+\frac{5}{2}$	$+\frac{7}{2}$
ϕ_4	$-4\rightarrow-4$	$-\frac{20}{7}\rightarrow-2$	$-\frac{12}{7}\rightarrow-1$	$-\frac{4}{7}\rightarrow0$	$\frac{4}{7}\rightarrow1$	$\frac{12}{7}\rightarrow2$	$\frac{20}{7}\rightarrow3$	$4\rightarrow4$
ϕ_3		$-\frac{15}{7}\rightarrow-3$	$-\frac{9}{7}\rightarrow-2$	$-\frac{3}{7}\rightarrow-1$	$\frac{3}{7}\rightarrow0$	$\frac{9}{7}\rightarrow1$	$\frac{15}{7}\rightarrow2$	
Sum	$-4\rightarrow-4$	$-5\rightarrow-5$	$-3\rightarrow-3$	$-1\rightarrow-1$	$1\rightarrow1$	$3\rightarrow3$	$5\rightarrow5$	$4\rightarrow4$

of m and k remains proportional to the field-strength during the complete transition from weak to strong fields.

In calculating the values of mg for strong fields, Pauli subdivides the equatorial quantum number m into two quantum numbers m_1 and μ, so that

$$m = m_1 + \mu.$$

Of these m_1 may have the 2K values of 0, ± 1, . . . $\pm(K - \frac{1}{2})$, and μ may in the case of even multiplicities have the 2R values of $\pm\frac{1}{2}$, $\pm\frac{3}{2}$, . . . $\pm(R - \frac{1}{2})$, and in the case of uneven multiplicities the 2R values of 0, ± 1, . . . $\pm(R - \frac{1}{2})$. The values of mg in strong fields are then simply given by

$$mg = m_1 + 2\mu = m + \mu = 2m - m_1 \quad . \quad . \quad (63)$$

The restriction to the possible combinations can now be expressed in these words. Only those transitions can take place in which μ remains unchanged. This means, when taken in conjunction with the selection principle and rule of polarisation, that the Zeeman pattern must be a normal triplet in the limiting case of a strong field.

We may now turn once again to Landé's interval factor γ which was introduced above.[1] Landé shows in the first place that the values of this factor for weak fields are given by

$$\gamma_w = \frac{I^2 + \frac{1}{4} - R^2 - K^2}{2RK} \quad . \quad . \quad . \quad (64)$$

and these are set forth in Table CLXX., which is the companion to Table CLV., which contains the values of g.

If follows at once from formula (64) that the interval between two members of a multiple term (which have the same values of R and K) is proportional to the difference between the values of γ for those two members. We have, therefore, the following expression of Landé's interval rule $\Delta\nu_{II'} - \Delta\nu_I = \Delta\nu_{I'} = (\gamma - \gamma')\omega$, and is proportional to $I^2 - I'^2$. Again, formula (63) fixes the optical centre of gravity of the multiple term from which we may picture arms of length γ reaching

[1] *Zeitsch. für Phys.*, **19**, 112 (1923).

TABLE CLXX.

$\Delta\nu =$ 1 : 2 : 3 : 4 : 5 : 6 : 7 — $\frac{3}{2} : \frac{5}{2} : \frac{7}{2} : \frac{9}{2} : \frac{11}{2} : \frac{13}{2} : \frac{15}{2} = \Delta$

$I =$ $\frac{1}{2}$ $\frac{3}{2}$ $\frac{5}{2}$ $\frac{7}{2}$ $\frac{9}{2}$ $\frac{11}{2}$ $\frac{13}{2}$ $\frac{15}{2}$ — 1 2 3 4 5 6 7 8 $= I$

Singlets, R = $\frac{1}{2}$

K	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$	$\frac{9}{2}$
$\frac{1}{2}$	0				
$\frac{3}{2}$		0			
$\frac{5}{2}$			0		
$\frac{7}{2}$				0	
$\frac{9}{2}$					0

Doublets, R = $\frac{2}{2}$

K	1	2	3	4	5	6	7	8
$\frac{1}{2}$	0							
$\frac{3}{2}$	$-\frac{2}{3}$	$\frac{1}{3}$						
$\frac{5}{2}$		$-\frac{3}{5}$	$\frac{2}{5}$					
$\frac{7}{2}$			$-\frac{4}{7}$	$\frac{3}{7}$				
$\frac{9}{2}$				$-\frac{5}{9}$	$\frac{4}{9}$			

Triplets, R = $\frac{3}{2}$

$\frac{1}{2}$		0			
$\frac{3}{2}$	$-\frac{8}{9}$	$-\frac{4}{9}$	$\frac{4}{9}$		
$\frac{5}{2}$		$-\frac{12}{15}$	$-\frac{4}{15}$	$\frac{8}{15}$	
$\frac{7}{2}$			$-\frac{16}{21}$	$-\frac{4}{21}$	$\frac{12}{21}$
$\frac{9}{2}$				$-\frac{20}{27}$	$-\frac{4}{27}$	$\frac{16}{27}$

Quartets, R = $\frac{4}{2}$

$\frac{1}{2}$			0			
$\frac{3}{2}$	$-\frac{5}{6}$	$-\frac{2}{6}$	$\frac{3}{6}$			
$\frac{5}{2}$	$-\frac{9}{10}$	$-\frac{6}{10}$	$-\frac{1}{10}$	$\frac{6}{10}$		
$\frac{7}{2}$		$-\frac{12}{14}$	$-\frac{7}{14}$	0	$\frac{9}{14}$	
$\frac{9}{2}$		$-\frac{15}{18}$	$-\frac{8}{18}$	$\frac{1}{18}$	$\frac{12}{18}$	

Quintets, R = $\frac{5}{2}$

$\frac{1}{2}$			0				
$\frac{3}{2}$		$-\frac{12}{15}$	$-\frac{4}{15}$	$\frac{8}{15}$			
$\frac{5}{2}$	$-\frac{24}{25}$	$-\frac{20}{25}$	$-\frac{12}{25}$	0	$\frac{16}{25}$		
$\frac{7}{2}$		$-\frac{32}{35}$	$-\frac{24}{25}$	$-\frac{12}{35}$	$\frac{4}{35}$	$\frac{24}{35}$	
$\frac{9}{2}$			$-\frac{40}{45}$	$-\frac{28}{45}$	$-\frac{12}{45}$	$\frac{8}{45}$	$\frac{32}{45}$

Sextets, R = $\frac{6}{2}$

$\frac{1}{2}$			0				
$\frac{3}{2}$		$-\frac{7}{9}$	$-\frac{2}{9}$	$\frac{5}{9}$			
$\frac{5}{2}$	$-\frac{14}{15}$	$-\frac{11}{15}$	$-\frac{6}{15}$	$\frac{1}{15}$	$\frac{10}{15}$		
$\frac{7}{2}$	$-\frac{20}{21}$	$-\frac{17}{21}$	$-\frac{12}{21}$	$-\frac{5}{21}$	$\frac{4}{21}$	$\frac{15}{21}$	
$\frac{9}{2}$		$-\frac{25}{27}$	$-\frac{20}{27}$	$-\frac{13}{27}$	$-\frac{4}{27}$	$\frac{7}{27}$	$\frac{20}{27}$

Septets, R = $\frac{7}{2}$

$\frac{1}{2}$				0			
$\frac{3}{2}$			$-\frac{16}{21}$	$-\frac{4}{21}$	$\frac{12}{21}$		
$\frac{5}{2}$		$-\frac{32}{35}$	$-\frac{24}{35}$	$-\frac{12}{35}$	$\frac{4}{35}$	$\frac{24}{35}$	
$\frac{7}{2}$	$-\frac{48}{49}$	$-\frac{44}{49}$	$-\frac{36}{49}$	$-\frac{24}{49}$	$-\frac{8}{49}$	$\frac{12}{49}$	$\frac{36}{49}$
$\frac{9}{2}$		$-\frac{60}{63}$	$-\frac{52}{63}$	$-\frac{40}{63}$	$-\frac{24}{63}$	$\frac{4}{63}$	$\frac{20}{63}$	$\frac{48}{63}$

Octets, R = $\frac{8}{2}$

$\frac{1}{2}$					0			
$\frac{3}{2}$				$-\frac{9}{12}$	$-\frac{2}{12}$	$\frac{7}{12}$		
$\frac{5}{2}$			$-\frac{18}{20}$	$-\frac{13}{20}$	$-\frac{6}{20}$	$\frac{3}{20}$	$\frac{14}{20}$	
$\frac{7}{2}$		$-\frac{27}{28}$	$-\frac{24}{28}$	$-\frac{19}{28}$	$-\frac{12}{28}$	$-\frac{3}{28}$	$\frac{8}{28}$	$\frac{21}{28}$
$\frac{9}{2}$	$-\frac{35}{36}$	$-\frac{32}{36}$	$-\frac{27}{36}$	$-\frac{20}{36}$	$-\frac{11}{36}$	0	$\frac{13}{36}$	$\frac{28}{36}$

$I =$ $\frac{1}{2}$ $\frac{3}{2}$ $\frac{5}{2}$ $\frac{7}{2}$ $\frac{9}{2}$ $\frac{11}{2}$ $\frac{13}{2}$ $\frac{15}{2}$ — 1 2 3 4 5 6 7 8 $= I$

$\Delta\nu =$ 1 : 2 : 3 : 4 : 5 : 6 : 7 — $\frac{3}{2} : \frac{5}{2} : \frac{7}{2} : \frac{9}{2} : \frac{11}{2} : \frac{13}{2} : \frac{15}{2} = \Delta$

out and carrying the term members as weights. The weight of each member is the number of magnetic terms it gives, that is to say 2I. There will exist a complete balance between all these weights for any one multiple term with definite values of R and K, that is to say, the sum of all values of $2I\gamma_w$ for the term will be zero, or

$$\sum_{I} 2I\gamma_w = 0,$$

when R and K are constant and I varies from $|R + K| - \frac{1}{2}$ to $|R - K| + \frac{1}{2}$. As an example of this we may take the *d* term of the quartet system ($R = \frac{4}{2}$, $K = \frac{5}{2}$).

The values of γ_w and 2I and their products are given in Table CLXXI.

TABLE CLXXI.

γ_w.	2I.	$2I\gamma_w$.
$-\frac{9}{10}$	2	$-\frac{18}{10}$
$-\frac{6}{10}$	4	$-\frac{24}{10}$
$-\frac{1}{10}$	6	$-\frac{6}{10}$
$+\frac{6}{10}$	8	$+\frac{48}{10}$

and as may be seen the sum of the values of $2I\gamma_w$ is equal to zero.

The position of the optical centre of gravity (Voigt's Schwerpunkt) can of course be found at once from the values of γ_w, and as an instance we may take the D lines of sodium. The values of γ_w are $-\frac{2}{3}$ and $+\frac{1}{3}$ for the two π terms, and consequently the position lies at two-thirds of the interval between the lines measured from the D_1 line. This was indicated in Fig. 38 on p. 381.

Landé deals with the value of γ_s for strong fields, and he shows by analogy with the Pauli method of calculating the values of *g* for strong fields the values of γ_s are given by

$$\gamma_s = \frac{m_1}{R} \cdot \frac{\mu}{K}.$$

The values of m_1 and μ are as follows:—

$$\left.\begin{array}{lll} m_1 = I - K, & \mu = m - (I - R), & \text{when } m \geqq R - K \\ m_1 = m - (R - I), & \mu = R - I, & \text{when } m \leqq R - K \end{array}\right\} \quad (65)$$

In Table CLXXII. are given the values of mg and γ for weak and strong fields for singlet, doublet, triplet, and quartet terms, these being taken from Pauli's and Landé's papers.[1] The upper figures in each case give the change in mg in passing from weak to strong fields, whilst the lower figures give the corresponding changes in the values of γ.

[1] See also *Zeemaneffekt und Multipletstruktur der Spektrallinien*, p. 70, E. Back and A. Landé, Julius Springer, Berlin, 1925.

TABLE CLXXII.

Singlet Terms, $R = \frac{1}{2}$.

$m =$	-2	-1	0	1	2
K I					
1 1			0 → 0		
2 2			0 → 0		
3 3		−1 → −1	0 → 0	1 → 1	
2 2		0 → 0	0 → 0	0 → 0	
5 5	−2 → −2	−1 → −1	0 → 0	1 → 1	2 → 2
2 2	0 → 0	0 → 0	0 → 0	0 → 0	0 → 0

Doublet Terms, $R = \frac{2}{2}$.

$m =$	$-\frac{5}{2}$	$-\frac{3}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$
K I						
1 1			−1 → −1	1 → 1		
2 1			0 → 0	0 → 0		
3/2 (2)		−2 → −2	$-\frac{2}{3}$ → 0	$\frac{2}{3}$ → 1	2 → 2	
		$\frac{1}{3}$ → $\frac{1}{3}$	$\frac{1}{3}$ → $-\frac{1}{3}$	$\frac{1}{3}$ → 0	$\frac{1}{3}$ → $\frac{1}{3}$	
3/2 (1)			$-\frac{1}{3}$ → −1	$\frac{1}{3}$ → 0		
			$-\frac{2}{3}$ → 0	$-\frac{2}{3}$ → $-\frac{1}{3}$		
5/2 (3)	−3 → −3	$-\frac{9}{5}$ → −1	$-\frac{3}{5}$ → 0	$\frac{3}{5}$ → 1	$\frac{9}{5}$ → 2	3 → 3
	$\frac{2}{5}$ → $\frac{2}{5}$	$\frac{2}{5}$ → $-\frac{2}{5}$	$\frac{2}{5}$ → $-\frac{1}{5}$	$\frac{2}{5}$ → 0	$\frac{2}{5}$ → $\frac{1}{5}$	$\frac{2}{5}$ → $\frac{2}{5}$
5/2 (2)		$-\frac{6}{5}$ → −2	$-\frac{2}{5}$ → −1	$\frac{2}{5}$ → 0	$\frac{6}{5}$ → 1	
		$-\frac{3}{5}$ → $\frac{1}{5}$	$-\frac{3}{5}$ → 0	$-\frac{3}{5}$ → $-\frac{1}{5}$	$-\frac{3}{5}$ → $-\frac{2}{5}$	

TABLE CLXXII.—*Continued.*

TRIPLET TERMS, $R = \frac{3}{2}$.

$m =$	-3.	-2.	-1.	0.	1.	2.	3.
K I							
$\frac{1}{2}$ $\frac{3}{2}$			$-2 \to -2$ $0 \to 0$	$0 \to 0$ $0 \to 0$	$2 \to 2$ $0 \to 0$		
$\frac{5}{2}$		$-3 \to -3$ $\frac{4}{9} \to \frac{4}{9}$	$-\frac{3}{2} \to -1$ $\frac{4}{9} \to 0$	$0 \to 1$ $\frac{4}{9} \to -\frac{4}{9}$	$\frac{3}{2} \to 2$ $\frac{4}{9} \to 0$	$3 \to 3$ $\frac{4}{9} \to \frac{4}{9}$	
$\frac{3}{2}$ $\frac{3}{2}$			$-\frac{3}{2} \to -2$ $-\frac{4}{9} \to 0$	$0 \to 0$ $-\frac{4}{9} \to 0$	$\frac{3}{2} \to 1$ $-\frac{4}{9} \to 0$		
$\frac{1}{2}$				$0 \to -1$ $-\frac{8}{9} \to -\frac{4}{9}$			
$\frac{7}{2}$	$-4 \to -4$ $\frac{8}{15} \to \frac{8}{15}$	$-\frac{8}{3} \to -2$ $\frac{8}{15} \to 0$	$-\frac{4}{3} \to 0$ $\frac{8}{15} \to -\frac{8}{15}$	$0 \to 1$ $\frac{8}{15} \to -\frac{4}{15}$	$\frac{4}{3} \to 2$ $\frac{8}{15} \to 0$	$\frac{8}{3} \to 3$ $\frac{8}{15} \to \frac{4}{15}$	$4 \to 4$ $\frac{8}{15} \to \frac{8}{15}$
$\frac{5}{2}$ $\frac{5}{2}$		$-\frac{14}{6} \to -3$ $-\frac{4}{15} \to \frac{4}{15}$	$-\frac{7}{6} \to -1$ $-\frac{4}{15} \to 0$	$0 \to 0$ $-\frac{4}{15} \to 0$	$\frac{7}{6} \to 1$ $-\frac{4}{15} \to 0$	$\frac{14}{6} \to 2$ $-\frac{4}{15} \to 0$	
$\frac{3}{2}$			$-\frac{1}{2} \to -2$ $-\frac{12}{15} \to 0$	$0 \to -1$ $-\frac{12}{15} \to -\frac{4}{15}$	$\frac{1}{2} \to 0$ $-\frac{12}{15} \to -\frac{8}{15}$		

TABLE CLXXII.—*Continued.*

QUARTET TERMS, $R = \frac{4}{2}$.

$m =$	$-\frac{7}{2}$.	$-\frac{5}{2}$.	$-\frac{3}{2}$.	$-\frac{1}{2}$.	$\frac{1}{2}$.	$\frac{3}{2}$.	$\frac{5}{2}$.
K I							
$\frac{1}{2}$ 2			$-3 \to -3$ $0 \to 0$	$-1 \to -1$ $0 \to 0$	$1 \to 1$ $0 \to 0$	$3 \to 3$ $0 \to 0$	
3		$-4 \to -4$ $\frac{1}{2} \to \frac{1}{2}$	$-\frac{12}{5} \to -2$ $\frac{1}{2} \to \frac{1}{6}$	$-\frac{4}{5} \to 0$ $\frac{1}{2} \to -\frac{1}{6}$	$\frac{4}{5} \to 2$ $\frac{1}{2} \to -\frac{1}{2}$	$\frac{12}{5} \to 3$ $\frac{1}{2} \to 0$	$4 \to 4$ $\frac{1}{2} \to \frac{1}{2}$
$\frac{3}{2}$ 2			$-\frac{39}{15} \to -3$ $-\frac{1}{3} \to 0$	$-\frac{13}{15} \to -1$ $-\frac{1}{3} \to 0$	$\frac{13}{15} \to 1$ $-\frac{1}{3} \to 0$	$\frac{39}{15} \to 2$ $-\frac{1}{3} \to \frac{1}{6}$	
1				$-\frac{4}{3} \to -2$ $-\frac{5}{6} \to -\frac{1}{2}$	$\frac{4}{3} \to 0$ $-\frac{5}{6} \to -\frac{1}{6}$		
4	$-5 \to -5$ $\frac{3}{5} \to \frac{3}{5}$	$-\frac{25}{7} \to -3$ $\frac{3}{5} \to \frac{1}{5}$	$-\frac{15}{7} \to -1$ $\frac{3}{5} \to -\frac{1}{5}$	$-\frac{5}{7} \to 1$ $\frac{3}{5} \to -\frac{3}{5}$	$\frac{5}{7} \to 2$ $\frac{3}{5} \to -\frac{3}{10}$	$\frac{15}{7} \to 3$ $\frac{3}{5} \to 0$	$\frac{25}{7} \to 4$ 5 $\frac{3}{5} \to \frac{3}{10}$ $\frac{3}{5}$
3		$-\frac{120}{35} \to -4$ $-\frac{1}{10} \to \frac{3}{10}$	$-\frac{72}{35} \to -2$ $-\frac{1}{10} \to \frac{1}{10}$	$-\frac{24}{35} \to 0$ $-\frac{1}{10} \to -\frac{1}{10}$	$\frac{24}{35} \to 1$ $-\frac{1}{10} \to 0$	$\frac{72}{35} \to 2$ $-\frac{1}{10} \to \frac{1}{10}$	$\frac{120}{35} \to 3$ $-\frac{1}{10} \to \frac{1}{5}$
$\frac{5}{2}$							
2			$-\frac{9}{5} \to -3$ $-\frac{3}{5} \to 0$	$-\frac{3}{5} \to -1$ $-\frac{3}{5} \to 0$	$\frac{3}{5} \to 0$ $-\frac{3}{5} \to -\frac{1}{10}$	$\frac{9}{5} \to 1$ $-\frac{3}{5} \to -\frac{1}{5}$	
1				$0 \to -2$ $-\frac{9}{10} \to -\frac{3}{10}$	$0 \to -1$ $-\frac{9}{10} \to -\frac{3}{5}$		

It may be seen from Table CLXXII. that the same principle of permanence of sums applies to the values of γ as to the values of g. The sum of the values of γ_s for all the members of a multiple term (with m, R, and K the same) is equal to the sum of the values of γ_w for those members. For example, in the diffuse term of the quartet system ($R = \frac{4}{2}$, $K = \frac{5}{2}$) we have for $m = \frac{1}{2}$

$$\tfrac{3}{5} - \tfrac{1}{10} \quad - \tfrac{3}{5} - \tfrac{9}{10} = - \tfrac{3}{10} \quad + 0 - \tfrac{1}{10} - \tfrac{3}{5} = - 1.$$

This can be expressed by

$$\sum_{1} \gamma_w = \sum_{1} \gamma_s$$

or

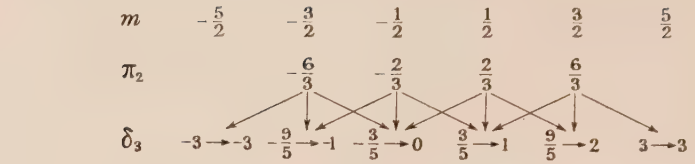
$$\sum_{1} (\gamma_w - \gamma_s) = 0.$$

It is of great interest to follow the changes which must take place in the Zeeman patterns of a given multiplet as the magnetic field is increased from very weak to very strong. These changes can readily be calculated from the values of mg given in Table CLXXII. The Zeeman patterns which are obtained with weak fields, that is to say, fields which are weak as regards both the combining terms, have already been discussed in some detail. As the magnetic field is increased the first effect to be observed will be a distortion of the symmetry of the Zeeman patterns, this being the first indication of an incipient Paschen-Back effect.

Since in general the members of one of the combining terms are closer together than the members of the other term, the former term will be the first to be influenced by the increase in the strength of the field. The first case to consider, therefore, is that in which the magnetic field is very weak with respect to one term and moderately strong with respect to the other term. As an example we may take the $\pi_i \delta_i$ combination of the doublet system, and, since the δ_i levels are closer together than the π_i levels, we may assume a field strength which is very weak as regards the latter and moderately strong as regards the former. In this case the values of mg for the two π levels will be those already given for very weak fields, but those for the two δ levels will lie somewhere between those for very weak and those for very strong fields. In Table CLXXIII. are given the combination schemes for the three lines of the diffuse doublet, the values of mg for both weak and strong fields being given in the case of the δ terms. In deriving the final Zeeman patterns both these values are used as shown in Table CLXXIII.

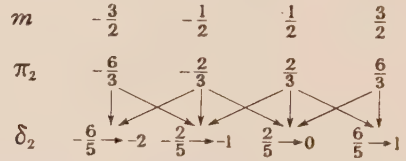
In the Zeeman pattern which is actually observed the various components will lie somewhere between the two extreme positions which are given for each. In other words, a distorted and unsymmetrical pattern will be obtained, the amount of distortion increasing with the strength of the field.

TABLE CLXXIII.


m
$-\frac{5}{2}$ $-\frac{3}{2}$ $-\frac{1}{2}$ $\frac{1}{2}$ $\frac{3}{2}$ $\frac{5}{2}$
π_2
$-\frac{6}{3}$ $-\frac{2}{3}$ $\frac{2}{3}$ $\frac{6}{3}$
δ_3
$-3 \rightarrow -3$ $-\frac{9}{5} \rightarrow -1$ $-\frac{3}{5} \rightarrow 0$ $\frac{3}{5} \rightarrow 1$ $\frac{9}{5} \rightarrow 2$ $3 \rightarrow 3$

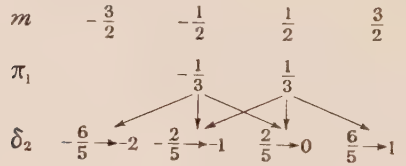
$-21 \rightarrow -30, -19 \rightarrow -25, -17 \rightarrow -20, -15 \rightarrow -15, (-3 \rightarrow -15), (-1 \rightarrow -10), (1 \rightarrow -5), (3 \rightarrow 0), 15 \rightarrow 15, 17 \rightarrow 15, 19 \rightarrow 10, 21 \rightarrow 15$

15



$-24 \rightarrow -15, -16 \rightarrow -10, -8 \rightarrow -5, (-12 \rightarrow 0), (-4 \rightarrow 5), (12 \rightarrow 15), 8 \rightarrow 20, 16 \rightarrow 25, 24 \rightarrow 30$

15



$-13 \rightarrow -10, -11 \rightarrow -5, (-1 \rightarrow 5), (1 \rightarrow 10), 11 \rightarrow 20, 13 \rightarrow 25$

15

The foregoing is one of the simpler cases of the incipient Paschen-Back effect. As can readily be understood the distortion will be greatly increased if the levels of both the terms are sufficiently close together to be affected, that is to say, if the magnetic field is moderately strong with respect to both terms.

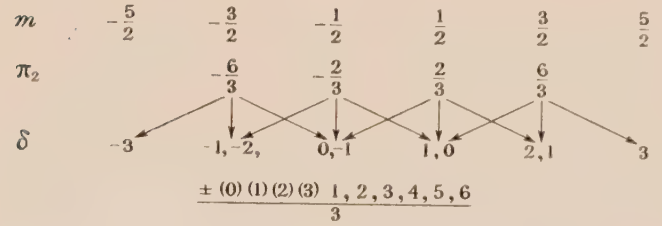
The next case we may consider is that in which the field is very strong as regards one term and very weak as regards the other. This condition gives what is known as the partial Paschen-Back effect and, although we may again deduce the Zeeman patterns of the $\pi_i\delta_i$ lines, it is not convenient to use the values given in Table CLXXIII. The reason for this is that the δ_3 and δ_2 terms can no longer be considered as separate entities but as a single δ unit. Further, owing to the existence of the external field the inner quantum number selection principle no longer holds and the combination $\pi_1\delta_3$ now occurs. The values of mg for the δ unit are given in Table CLXXIV. those derived from δ_3 being given first.

The combinations between the δ values given in Table CLXXIV. and the π_2 and π_1 levels are given in Table CLXXV., the usual rules as to transitions in m being obeyed.

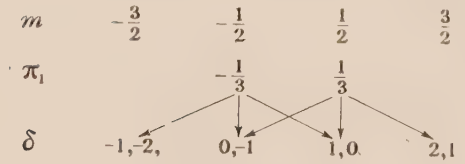
TABLE CLXXIV.

m	$-\frac{5}{2}$	$-\frac{3}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$
δ	-3	$-1, -2$	$0, -1$	$1, 0$	$2, 1$	3

TABLE CLXXV.



$$\frac{\pm (0)\,(1)\,(2)\,(3)\;\;1, 2, 3, 4, 5, 6}{3}$$

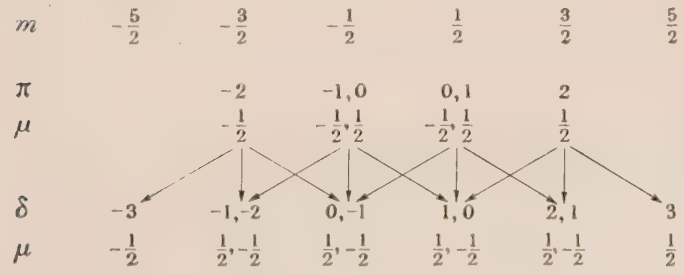


$$\frac{\pm (1)\,(2)\;\;1, 2, 4, 5}{3}$$

As can be seen the Zeeman patterns have again become symmetrical. Observation has shown that all of the calculated components do not make their appearance, and it would therefore seem that there must exist a new selection principle. This, however, has not as yet been formulated.

Lastly, we come to the complete Paschen-Back effect in which the two π terms as well as the two δ terms are completely changed

TABLE CLXXVI.



$$\pm (0)\;1$$

by a very strong field. We then have the values of mg for the π and δ units given in Table CLXXII. It must now be remembered that in this case, according to the principle enunciated by Pauli, combination only occurs between those levels which have the same values of μ. These are found from equation (63),

$$\mu = mg - m,$$

and are given in Table CLXXVI. under each value of mg.

The Zeeman Effect in Multiplets of Higher Orders of Complexity.—The only spectrum of a higher order of complexity which has been examined in the magnetic field is that of neon, and the results seem to show that Runge's law and probably also Preston's law are not obeyed. This divergence from the two standard laws of magnetic resolution was theoretically deduced by Heisenberg,[1] who also suggested that Runge's law in the case of simple multiplets is only approximate. On the other hand, Back concludes from his measurements of the neon spectrum that in the first members of the s and p term series all the values of the resolution factor g are multiples of the Runge fraction $\frac{1}{3 0}$.

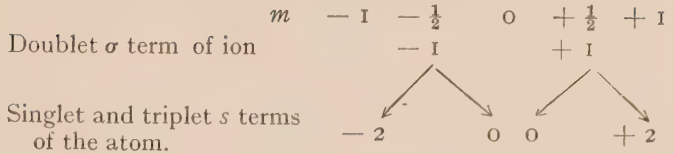
If Heisenberg's deduction is correct, then, as Landé[2] points out, all the values of g for terms of higher order of complexity than the first are not rational and constant with varying total quantum number n. On the other hand, the values of g for terms having the same values of K and I give rational and constant sums. Thus the three neon terms, p_4, p_6, and p_8 $(I = \frac{5}{2})$[3] possess values of g which are irrational and vary with n, but which give the rational and constant sum $\frac{11}{3}$. This g-sum is to be divided in an irrational and variable manner amongst the three p terms, this being indicated by the expression $\frac{11}{3} : 3$. Rational and constant values of g only exist when there is only one term having a particular value of I. Thus in the case of neon there is only one p-term with $I = \frac{7}{2}$ and the value of g for this term is $\frac{4}{3}$.

Landé gives two methods of calculating the values of g and g-sums, the first of these being a combination of the principle of branching[4] and the permanence of g-sums[5] in simple multiplets. He illustrates this method with simple multiplets and takes the case of an ion having a doublet σ term with the resolution

m	$-\frac{1}{2}$	$+\frac{1}{2}$
mg	-1	$+1$.

If this ion captures another electron to give an s term, then the values of m branch into $m \pm \frac{1}{2}$ whilst those of mg branch into $mg \pm 1$.

[1] *Zeitsch. für Phys.*, **26**, 291 (1924).
[2] *Ann. der Phys.*, **76**, 273 (1925).
[3] This is Paschen's notation (see p. 213).
[4] Landé and Heisenberg, *Zeitsch. für Phys.*, **25**, 279 (1924); see also p. 212.
[5] Pauli, *ibid.*, **16**, 155 (1923); see p. 382.



In this way we obtain

Singlet *s* term. $mg = 0$,

Triplet *s* term. $mg = -2,\ 0,\ +2$

these values being the same in weak and strong fields. The resolution of the *p*, *d*, and *f* terms in strong fields is obtained by increasing the values of *m* and *mg* for the *s* terms by 0 and ± 1; 0, ± 1, ± 2; and 0, ± 1, ± 2, ± 3, respectively. We thus obtain for strong fields the values shown in Table CLXXVII.

TABLE CLXXVII.

SINGLET.

m	− 2	− 1	0	+ 1	+ 2
S			0		
P		− 1	0	+ 1	
D	− 2	− 1	0	+ 1	+ 2

TRIPLET.

m	− 3	− 2	− 1	0	1	2	3
s			− 2	0	+ 2		
p_{012}		− 3	− 2, − 1	− 1, 0, + 1	+ 1, + 2	+ 3	
d_{123}	− 4	− 3, − 2	− 2, − 1, 0	− 1, 0, + 1	0, + 1, + 2	+ 2, + 3	+ 4

In order to calculate the values of *mg* for weak fields the law of permanence of *g*-sums is utilised. The values of mg_s in each compartment are added together and the resulting sums are divided up in such a way that the new terms mg_w are the products of *m* into the factors g_w. This subdivision of the *g*-sums gives the results shown in Table CLXXVIII.

TABLE CLXXVIII.

SINGLET ; mg_w.

m	− 2	− 1	0	+ 1	+ 2
S			0		
P		− 1	0	+ 1	
D	− 2	− 1	0	+ 1	+ 2

Triplet mg_w

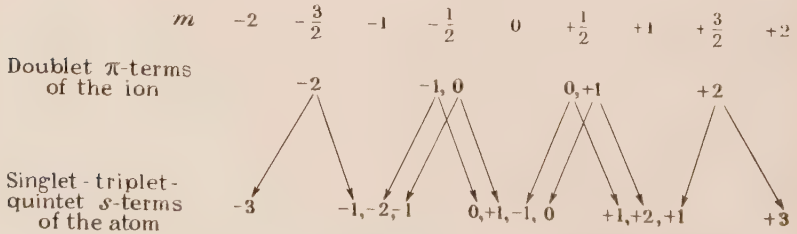
m	−3	−2	−1	0	+1	+2	+3
s			-2	0	+2		
p_{012}		$-\frac{6}{2}$	$-\frac{3}{2}, -\frac{3}{2}$	0, 0, 0	$+\frac{3}{2}, +\frac{3}{2}$	$+\frac{6}{2}$	
d_{123}	$-\frac{12}{3}$	$-\frac{8}{3}, -\frac{14}{6}$	$-\frac{4}{3}, -\frac{7}{6}, -\frac{1}{2}$	0, 0, 0	$+\frac{1}{2}, +\frac{7}{6}, +\frac{4}{3}$	$+\frac{14}{6}, +\frac{8}{3}$	$+\frac{12}{3}$

As can be seen at once these give the known values of g for weak fields.[1]

Landé calculates the values of g for the multiplet terms of the second order of complexity in exactly the same way and gives as his example the case of neon, starting from the doublet π term of the neon ion which shows the following resolution in strong fields :—

m	$-\frac{3}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{3}{2}$
mg	− 2	− 1, 0	0, + 1	+ 2

If the capture of a further electron yields an s term of the neon atom, then by exactly the same branching of m and mg, we have



The resolution of the p, d, and f terms is obtained exactly as before by the branching of the values of m and mg for the s terms, with the result as shown in Table CLXXIX.

[1] See p. 367.

TABLE CLXXIX.

1335-SYSTEM ; mg_s.

m	−3	−2	−1	0	+1	+2	+3
s		−3	−1, −2, −1	0, +1, −1, 0	+1, +2, +1	+3	
p	−4	−3, −3, −2, −2	0, −2, −2, −1, −1, −1, −1, −1	−1, −1, 0, 0, 0, 0, 0, 0, +1, +1	0, +2, +2, +2, +1, +1, +1, +1	+3, +3, +2, +2	+4

In order to obtain the values of mg in weak fields, the values of mg_s in each compartment are added together to give the sums of mg_w. As before these sums should be divided up in such a way that the new terms mg_w are the products of m into the factors g_w, but this is no longer free from ambiguity, since it is only the sums which are certain. Where there is more than one term having the same value of I it is not possible to evaluate the individual numbers, mg_w. Adopting the conventional method mentioned above we divide up the sums in the manner set forth in Table CLXXX.

TABLE CLXXX.

1335-SYSTEM ; mg_w.

m	−3	−2	−1	0	+1	+2	+3
s		$-\frac{6}{2}$	$-\frac{3}{2}, -\frac{5}{2}$: 2	0, 0, 0, 0	$+\frac{5}{2}$: 2, $+\frac{3}{2}$	$+\frac{6}{2}$	
p	$-\frac{12}{3}$	$-\frac{8}{3}, -\frac{22}{3}$: 3	$-\frac{4}{3}, -\frac{11}{3}$: 3, −5 : 4	0, 0, 0, 0, 0, 0, 0, 0, 0, 0	+5 : 4, $+\frac{11}{3}$: 3, $+\frac{4}{3}$	$+\frac{22}{3}$: 3, $+\frac{8}{3}$	$+\frac{12}{3}$

From this table the following values of g and g-sums are obtained for weak fields :—

I	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$	
s	$\frac{0}{0}$	$\frac{5}{2}$: 2	$\frac{3}{2}$		n^{1335}
p	$\frac{0}{0}$: 2	5 : 4	$\frac{11}{3}$: 3	$\frac{4}{3}$	

The second method used by Landé for the calculation of values of g_w for the multiplet terms of higher orders of complexity is based on the ideal values which Heisenberg conceives g_w would have in the limit when the total quantum number n is very large. He exemplifies this method once again for the case of neon and employs the following argument. If the doublet π term of the neon ion ($R = \frac{3}{2}$ and $K = \frac{3}{2}$) captures another electron with $K = \frac{1}{2}$, the resulting s terms of the neon atom should exhibit the same magnetic resolution as the terms obtained when an ion with $R = \frac{3}{2}$ and $K = \frac{1}{2}$ captures an electron with $K = \frac{3}{2}$. The latter terms, however, with $R = \frac{3}{2} + \frac{1}{2}$ and $K = \frac{3}{2}$ will be the p terms of the singlet and triplet systems of the first order of complexity, the values of g_w being 1, and $\frac{0}{0}$, $\frac{3}{2}$, $\frac{3}{2}$, respectively. According to Heisenberg, the ideal values

of g_w for the four s terms of the neon atom are not all unity, nor are they equal to 2 as in the case of the s terms of first order multiplets. From formula (31) on p. 332 the latter are given by

$$g = 1 + \delta,$$

where

$$\delta = \frac{I^2 - \frac{1}{4} + R^2 - K^2}{2(I^2 - \frac{1}{4})}$$

and as for s terms $K = \frac{1}{2}$, $R = I$ it follows that $\delta = 1$ and $g = 2$. The ideal g-values of the four s terms of the neon atom ($\delta = 1$) are given by

$$g = 1, \qquad g = 1, \qquad g = 1 + \tfrac{1}{2}\delta, \qquad g = 1 + \tfrac{1}{2}\delta.$$

Using these ideal g values and deriving from them the ideal g values for the p and d terms of neon, we obtain the values shown in Table CLXXXI.

TABLE CLXXXI.

	Singlet, $R = \frac{1}{2}$	*Triplet*, $R = \frac{3}{2}$	*Triplet*, $R = \frac{3}{2}$	*Quintet*, $R = \frac{5}{2}$
s	$\frac{0}{0}$	1	$\frac{3}{2}$	$\frac{3}{2}$
p	1	$\frac{0}{0}$ 1 1	$\frac{0}{0}$ $\frac{5}{4}$ $\frac{5}{4}$	$\frac{7}{4}$ $\frac{17}{12}$ $\frac{4}{3}$
d	1	1 1 1	$\frac{3}{4}$ $\frac{13}{12}$ $\frac{7}{6}$	$\frac{0}{0}$ $\frac{5}{4}$ $\frac{5}{4}$ $\frac{5}{4}$ $\frac{5}{4}$
I	$\frac{1}{2}$ $\frac{3}{2}$ $\frac{5}{2}$	$\frac{1}{2}$ $\frac{3}{2}$ $\frac{5}{2}$ $\frac{7}{2}$	$\frac{1}{2}$ $\frac{3}{2}$ $\frac{5}{2}$ $\frac{7}{2}$	$\frac{1}{2}$ $\frac{3}{2}$ $\frac{5}{2}$ $\frac{7}{2}$ $\frac{9}{2}$

As will be seen the values for the s terms are the same as those obtained for the p terms when the order of capture of the electrons is reversed. These ideal g values are now arranged according to the values of I as shown in Table CLXXXII.

TABLE CLXXXII.

I	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$	$\frac{9}{2}$
s	$\frac{0}{0}$	1, $\frac{3}{2}$	$\frac{3}{2}$		
p	$\frac{0}{0}$, $\frac{0}{0}$	1, 1, $\frac{5}{4}$, $\frac{7}{4}$	1, $\frac{5}{4}$, $\frac{17}{12}$	$\frac{4}{3}$	
d	$\frac{0}{0}$	1, $\frac{3}{4}$, $\frac{5}{4}$	1, 1, $\frac{13}{12}$, $\frac{5}{4}$	1, $\frac{7}{6}$, $\frac{5}{4}$	$\frac{5}{4}$

Now the real values of g differ somewhat from these ideal values, but the sums of the real values equal the sums of the ideal values. The ideal values in each compartment of the above table are added together and the resulting sums are to be divided in an irrational manner as was done previously. This gives the values set forth in Table CLXXXIII., and they are identical with those calculated by the first method.

TABLE CLXXXIII.

I.	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$	$\frac{9}{2}$
s	$\frac{0}{0}$	$\frac{5}{2} : 2$	$\frac{3}{2}$		
p	$\frac{0}{0} : 2$	$5 : 4$	$\frac{11}{3} : 3$	$\frac{4}{3}$	
d	$\frac{0}{0}$	$3 : 3$	$\frac{13}{3} : 4$	$\frac{41}{12} : 3$	$\frac{5}{4}$

Landé gives a table of the values of g- and g-sums for the terms of four systems of multiplets of the second order, and this is reproduced in Table CLXXXIV.

TABLE CLXXXIV.

I	1	2	3	4	5	
s	$\frac{2}{3}$	$\frac{4}{3}$		n^{24}		
p	$\frac{8}{3} : 2$	$\frac{32}{15} : 2$	$\frac{6}{5}$			
d	$\frac{2}{3}$	$\frac{32}{15} : 2$	$\frac{72}{35} : 2$	$\frac{8}{7}$		
f		$\frac{4}{5}$	$\frac{72}{35} : 2$	$\frac{128}{63} : 2$	$\frac{10}{9}$	

I	1	2	3	4	5	6
s		$\frac{4}{5}$	$\frac{6}{5}$		n^{46}	
p	$\frac{2}{3}$	$\frac{32}{15} : 2$	$\frac{72}{35} : 2$	$\frac{8}{7}$		
d	$\frac{8}{3} : 2$	$\frac{32}{15} : 2$	$\frac{72}{35} : 2$	$\frac{128}{63} : 2$	$\frac{10}{9}$	
f	$\frac{2}{3}$	$\frac{32}{15} : 2$	$\frac{72}{35} : 2$	$\frac{128}{63} : 2$	$\frac{200}{99} : 2$	$\frac{12}{11}$

TABLE CLXXXIV.—*Continued.*

I	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$	$\frac{9}{2}$	$\frac{11}{2}$
s	$\frac{0}{0}$	$\frac{5}{2}:2$	$\frac{3}{2}$		n^{1335}_{neon}	
p	$\frac{0}{0}:2$	$5:4$	$\frac{11}{3}:3$	$\frac{4}{3}$		
d	$\frac{0}{0}$	$3:3$	$\frac{13}{3}:4$	$\frac{41}{12}:3$	$\frac{5}{4}$	
f		$\frac{1}{2}$	$\frac{17}{6}:3$	$\frac{25}{6}:4$	$\frac{33}{10}:3$	$\frac{6}{5}$

I	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$	$\frac{9}{2}$	$\frac{11}{2}$	$\frac{13}{2}$
s		$\frac{1}{2}$	$\frac{13}{6}:2$	$\frac{4}{3}$		n^{3557}	
p	$\frac{0}{0}$	$3:3$	$\frac{13}{3}:4$	$\frac{41}{12}:3$	$\frac{5}{4}$		
d	$\frac{0}{0}:2$	$5:4$	$\frac{13}{3}:4$	$\frac{25}{6}:4$	$\frac{33}{10}:3$	$\frac{6}{5}$	
f	$\frac{0}{0}$	$3:3$	$\frac{13}{3}:4$	$\frac{25}{6}:4$	$\frac{41}{10}:4$	$\frac{97}{30}:3$	$\frac{7}{6}$

The theoretical conclusions of Landé as to the values of g for the neon terms have been experimentally tested, so far as the s and p terms are concerned, by Back.[1] Observations of the Zeeman patterns given by the lines of this gas had previously been made by Lohman,[2] Takamine and Yamada,[3] and Nagaoka,[4] but these need not be detailed in view of the greater accuracy of Back's measurements. The method of the determination of the values of i and g has already been explained, and it is only necessary to give the values of g for the four s terms and the ten p terms. The nomenclature of these terms is that adopted by Paschen and dealt with in Chapter I., p. 213, the values of I and g being given in Table CLXXXV.

From the g values set forth in Table CLXXXV. it is possible at once to test the theoretical deductions made by Landé as to the values of the g-sums and of g for the single terms s_3, s_5, p_1, p_3, and p_9. The members of the three groups of terms

s_2, s_4	$I = \frac{3}{2}$,
p_2, p_5, p_7, p_{10}	$I = \frac{3}{2}$,
p_4, p_6, p_8	$I = \frac{5}{2}$,

[1] *Ann. der Phys.*, **76**, 317 (1925). [2] *Dissertation*, Halle, 1907.
[3] *Proc. Math. Phys. Soc.*, Tokyo, **7**, 277 (1914).
[4] *Proc. Phys. Soc.*, London, **28**, 83 (1921).

TABLE CLXXXV.

1 —	$\frac{3}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$\frac{5}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$	$\frac{3}{2}$
λ	s_2	s_3	s_4	s_5	p_1	p_2	p_3	p_4	p_5	p_6	p_7	p_8	p_9	p_{10}
7245 [1]			1·454											1·979
7032 [1]				1·501										1·988
6929 [1]	1·030									1·226				
6717	1·035								0·9908					
6678	1·037							1·298						
6598	1·034					1·335								
6532		0									0·6639			
6506		0	1·466									1·136		
6402				1·496									1·329	
6382			1·469								0·6689			
6334				1·497								1·139		
6304			1·462							1·229				
6266		0							0·9937					
6217				1·502							0·6758			
6163		0				1·339								
6143		0		1·499						1·233				
6128 [1]			1·455						0·9860					
6096			1·468					1·300						
6074			1·465				0							
6029			1·470			1·333	0							
5975 [1]				1·516					1·025					
5944				1·506				1·304						
5881				1·507		1·352								
5852	1·034				0									
Mean values	1·034	0	1·464	1·503	0	1·340	0	1·301	0·999	1·229	0·6695	1·137	1·329	1·984 [1]

[1] These lines were only measured in the first order, the accuracy being smaller.

have the same values of I as shown, and consequently, according to Landé, the sum of the values of g for each group should be a rational number. As shown in Table CLXXXIII., p. 397, the values of these g-sums should be $\frac{5}{2}$, 5, and $\frac{11}{3}$, respectively. In the upper part of Table CLXXXVI. the mean values of g found by Back are arranged according to the values of I and the sums of each of the three groups are given. As can be seen these agree exactly with the values calculated by Landé.

TABLE CLXXXVI.

		I.	g obs.	Σg calc.	Values of g expressed as Runge fractions.
Branched terms.	s_2	$\frac{3}{2}$	1·034		$1{\cdot}033 = \frac{31}{30}$
	s_4	$\frac{3}{2}$	1·464		$1{\cdot}467 = \frac{44}{30}$
		Sum	2·498	$\frac{5}{2} = 2{\cdot}500$	$\frac{5}{2} = \frac{75}{30}$
	p_4	$\frac{5}{2}$	1·301		$1{\cdot}300 = \frac{39}{30}$
	p_6	$\frac{5}{2}$	1·229		$1{\cdot}233 = \frac{37}{30}$
	p_8	$\frac{5}{2}$	1·137		$1{\cdot}133 = \frac{34}{30}$
		Sum	3·667	$\frac{11}{3} = 3{\cdot}667$	$\frac{11}{3} = \frac{110}{30}$
	p_2	$\frac{3}{2}$	1·3400		$1{\cdot}333 = \frac{40}{30}$
	p_5	$\frac{3}{2}$	0·9990		$1{\cdot}000 = \frac{30}{30}$
	p_7	$\frac{3}{2}$	0·6695		$0{\cdot}667 = \frac{20}{30}$
	p_{10}	$\frac{3}{2}$	1·9840		$2{\cdot}000 = \frac{60}{30}$
		Sum	4·9925	5·0	$5{\cdot}0 = \frac{150}{30}$
	s_3	$\frac{1}{2}$	$\frac{0}{0}$	$\frac{0}{0}$	0
	s_5	$\frac{5}{2}$	1·503	$\frac{3}{2}$	$\frac{3}{2} = \frac{45}{30}$
	p_1	$\frac{1}{2}$	$\frac{0}{0}$	$\frac{0}{0}$	0
	p_3	$\frac{1}{2}$	$\frac{0}{0}$	$\frac{0}{0}$	0
	p_9	$\frac{7}{2}$	1·329	$\frac{4}{3}$	$\frac{4}{3} = \frac{40}{30}$

In the lower part of Table CLXXXVI. are given the values of g experimentally found for the five single terms, and these again agree with the values calculated by Landé.

In his paper Landé stated that the g-sums are to be divided in an irrational manner between the terms composing the groups, but Back shows that in the first members of the series of s and p terms the values of g can all be expressed as rational numbers, namely multiples of the Runge fraction $\frac{1}{36}$. This is shown in the last column of Table CLXXXVI., the g-sums also being expressed in terms of the same fraction. This does not necessarily conflict with Landé's theory, since it is not possible from these investigations to say whether the values of g will be the same for the higher members of each series.

Apparatus and Experimental Methods.—In dealing with the experimental methods employed in the study of the magnetic resolutions of spectrum lines there come under consideration first the apparatus, that is to say, the light source, the electro-magnet, and the spectrograph, and second the measurement and calculation of the distribution of the components of each Zeeman pattern. The apparatus may be described first, and before any details are given a few general remarks may be made on the nature of the problem which faces any investigator in this most interesting field of work. The essential feature is the very fine structure of many Zeeman patterns, which necessitates the use of a spectrograph of high resolving power. In addition to this it must be remembered that in order that the full resolving power be utilised rigid control must be maintained on the magnetic field, which must be both homogeneous and constant. Then again, it is necessary that the spectrum lines in the absence of the field be as narrow and sharply defined as possible. Furthermore, the decrease in the effective intensity owing to the resolution into components necessitates longer exposures than is necessary in ordinary spectrum work, and this increases the importance of a constant temperature in the laboratory, which may readily be disturbed if the electro-magnet becomes warm during its use. The possible sources of trouble, therefore, are many, but during recent years the experimental technique has so far been advanced that the analysis of Zeeman patterns has reached a remarkable degree of accuracy. The truth of this statement may at once be justified by a reference to the work of Back on the magnetic resolution of the lines of manganese and neon.[1]

In describing the apparatus in detail we may first consider the magnet and then the light source which must be set up between the poles of the magnet. It will be obvious that the first object to be aimed at is the largest field possible, since the separation of the components of the Zeeman pattern is proportional thereto. In order that the definition of the components be the best possible it is equally evident that there are three additional requirements, namely,

[1] See pp. 343 and 398.

(1) that the field remain constant during the whole period of photographic observation, (2) that the field be homogeneous over the whole region in which the light emission takes place, and (3) that the temperature of the magnet remain constant during the whole exposure.

It is not possible to enter here into the theory and design of electro-magnets suitable for this type of work, but reference may be made to important papers by du Bois on the half-ring construction [1] and by Weiss on the rectangular form.[2] As regards the minimum field strength required, this depends on the type of spectrograph to be employed. It will be shown below that, except in special cases, the concave grating is the most convenient apparatus for general work, and with the largest instrument of this type a field of 35,000 to 40,000 Gauss is necessary to observe the resolution of the fine Zeeman patterns. Fields up to this strength were used by Paschen and Back in their work on the Paschen-Back effect, and by Back in his work on manganese, neon, etc.

The construction of a large electro-magnet has been described by Weiss.[3] An important feature is the use of copper tubing in place of wire for carrying the exciting current. The tubing is 6·4 mm. in external and 3·6 mm. in internal diameter, and it is capable of carrying 100 amperes, the whole being kept cool by water circulating through the coils. Each of the exciting coils is built up in five sections of 144 turns, which are connected in series for the current and in parallel for the water circulation. This use of copper tubing through which water is circulated prevents any heating of the apparatus during operation and as has already been pointed out this is an absolute necessity when long exposures are used. A constant field, moreover, is secured by reason of the fact that with constant temperature the resistance of the coils remains constant.

In order to observe the longitudinal Zeeman effect it is necessary that the poles of the magnet be bored so as to allow observations to be made through them. This, however, has the great disadvantage that it is prone to produce a field which is non-homogeneous, and for this reason it is customary to use solid pole pieces and only to observe the transverse effect. For this work the poles are fitted with conical pole pieces and the points of these cones are ground flat, the flat surface being from 5 to 7 mm. in diameter and the angle between the apices of the cones being 125°. In this way the magnetic field is concentrated on a cylindrical space within which the light source is placed. The distance between these plane surfaces is adjustable by means of a screw.

In the usual type of electro-magnet the core and the pole pieces are made of soft iron, the upper limit of the field being fixed by the saturation value of iron. Weiss showed that the alloy of iron and cobalt, Fe_2Co, has a saturation value 10 per cent. higher than that

[1] *Zeitsch. für Instrumentenkunde*, 1911, 376.
[2] *Journ. de Phys.*, **6**, 353 (1907).
[3] *Arch. des Sciences*, **44**, 464 (1917).

of iron. Although it is not possible to construct the whole core of this alloy, considerable advantage is obtained by using it for the ends of the pole pieces, an increase of 5 per cent. in the field being thus obtained.

Turning next to the light sources which are most suited for use in a strong field, it must be remembered that an electric discharge is readily affected by the field and a special technique is necessary to obtain the best results. The most usual light source is the spark discharge, and we are indebted to Back for a special method whereby excellent results may be obtained with certain metals.[2] The essential condition to be obtained is a discharge of sufficient intensity which gives the spectrum lines with the sharpest definition possible. In general this cannot be secured by the use of pure metallic electrodes, since the density of the metallic vapour in the spark tends to give broad and badly defined lines and in many cases self-reversal. Back points out that the best results are obtained by the use of an alloy of the required metal.

The electrodes consist of narrow thin strips which at one end have a circular disc of the same diameter as the flat end of the pole pieces of the magnet. These electrodes, which may be about 2 cm. long, are attached to brass rods cemented in glass tubes for convenience in mounting. It is of course necessary that the stand and clamps for holding these tubes have no iron in their construction. In mounting the electrodes they are set so that their terminal discs are exactly parallel to one another and the flat ends of the pole pieces of the magnet. In this way the whole of the air space between the discs will lie in a homogeneous magnetic field. In order to insulate the electrode discs from the pole pieces thin sheets of mica may be placed between them. This method of mounting is the most symmetrical possible and every spark discharge takes place in a homogeneous field.

As has already been said the material out of which the electrodes are made should be an alloy of the metal under investigation with some other metal such as zinc, cadmium, silver. As will be discussed below the strength of the field used in any observation is determined from the measurement of the resolution of lines which give normal triplets or a known definite pattern. For this reason the alloy should contain as one of its components a metal giving such standard lines.

In the case of the alkali metals, calcium, and strontium, alloys of which cannot be prepared in the usual way, the following method of preparing alloys with silver was used by Back. The electrode discs are now made of carefully purified gas carbon and coated with the silver alloy by dipping them into a fused mixture of the nitrates of silver and the metal required. 40 grams of silver nitrate are melted in a crucible and then 20 grams of sodium nitrate, for example,

[1] *Compt. Rendus*, **156**, 1764 (1913). [2] *Dissertation*, Tübingen, 1921.

are added and the whole melted together and well mixed. The temperature is then raised to the boiling-point of the mixture and the carbon electrodes which have previously been heated and cooled are dipped into the melt. Copious evolution of the oxides of nitrogen and carbon takes place and the electrodes become coated with a thick metallic layer. The discs are dried near the flame and the metallic layer rubbed with emery paper. For the purpose of obtaining standard lines a small fragment of aluminium nitrate may be added to the original melt, when the lines at $\lambda = 3944$ and 3961, which give the D_1 and D_2 types, will be obtained in the spectrum. This method can also be used with cadmium, zinc, magnesium, and aluminium.

When an alloy of the required metal cannot be prepared it is advisable to employ an entirely different method, since, although it is possible to use a carbon electrode coated with a layer of a fused salt, this, as a general rule, is not satisfactory. By his design of an intermittent arc in vacuo Back has succeeded in removing almost all the difficulties in obtaining a light source which satisfies the whole of the criteria demanded by the most exacting experimenter. So far as metallic spectra are concerned the main principle of this apparatus consists in a rotating brass rod which carries at its end a strip of metallic tungsten. This strip is bent so that during each revolution it touches an electrode of the metal under examination. At each contact an arc is formed between the two which is again broken after a very short interval of time. In view of the great value of this method the apparatus may be described in detail.[1]

Back prefaces his account of the apparatus with some general remarks which may well be quoted. The maximum sharpness of spectrum lines can only be secured with a light source in a vacuum, and the possible means of gaining this end are the vacuum tube, the vacuum spark discharge in series with an external spark gap in air, and the vacuum arc. The two first have certain disadvantages. The discharge in a vacuum tube across the lines of force is hindered by the field. The discharge shrinks to a thin thread which lies on one side of the capillary tube, the character of the discharge being similar to that obtained at higher pressures. If the capillary portion of the tube is placed parallel to the lines of force these disadvantages disappear, but there arises a danger of the want of homogeneity in the field (owing to the necessity for the use of hollow pole pieces). The vacuum spark suffers in intensity since most of the energy is used up in the external spark and in addition to this disturbances occur owing to the Stark effect.

The vacuum arc is free from these faults. If the discharge passes in a direction parallel to the lines of force a truly homogeneous field can be secured. Then, further, it has the advantage that the electrode carrying the metal under investigation can readily and quickly be changed. Lastly, there is the additional advantage that the vacuum

[1] *Ann. der Phys.*, **70**, 333 (1923).

arc in hydrogen under reduced pressure gives both the arc and spark lines of the metal. In the absence of the magnetic field, only the arc lines are obtained, but when the field is established the spark lines make their appearance with an intensity which often surpasses that of the arc lines. This change takes place even with the weakest

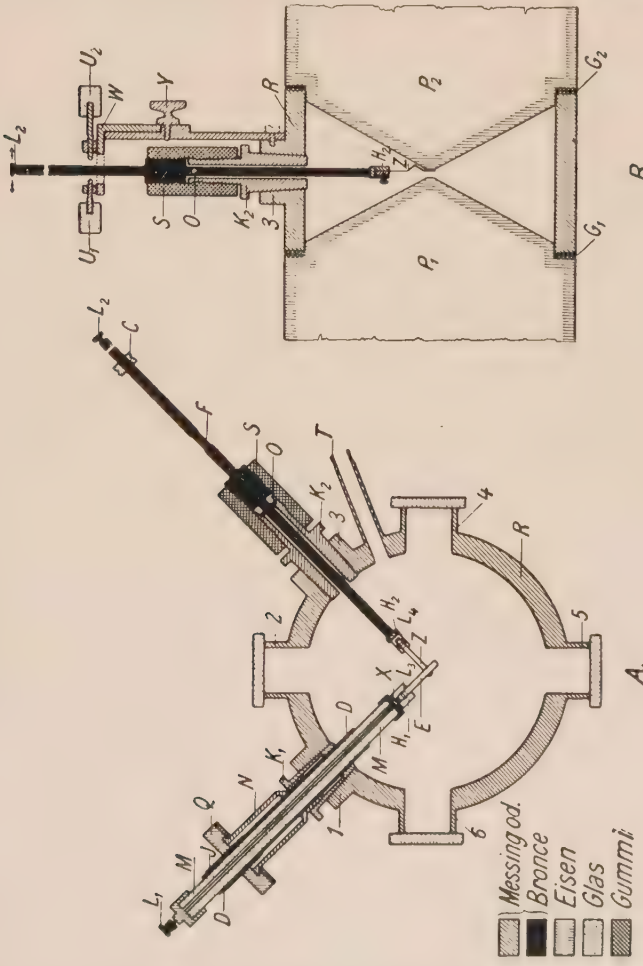


FIG. 39.
(From "Annalen der Physik," Vol. 70, p. 337, 1923.)

fields without increasing the potential of the discharge. The phenomenon gives a ready method of differentiating between the two types of lines.

The apparatus is shown in Fig. 39 where A is a section across the lines of force and B is a section through the axis of the pole pieces P_1 and P_2. R is a stout bronze cylinder and the two pole pieces are

recessed as shown so as to make a sliding fit. The junction is made air-tight by means of the rubber rings G_1 and G_2, and by the use of rings of different thicknesses it is possible to adjust the distance between the pole pieces to any desired amount. The bronze cylinder is provided with six side tubes, 1 to 6, and of these 2, 4, 5, and 6 have transparent windows cemented on for purpose of observation, whilst two, 1 and 3, are conical and into these the cones K_1 and K_2 are ground in. In addition to these there is a further side tube, T, which is attached to a mercury air pump. The two cones are bored centrally and carry the two electrodes, and of these that in K_1 is adjustable only in the direction of its length, whilst that in K_2 can only be rotated around its central axis. The construction of the K_1 electrode is so designed that the position of the end piece, E, which consists of the metal under examination, can be accurately adjusted and also that E may be changed during an observation without interrupting the magnetic field. The end piece E is attached by the electrode-holder H_1 and this in its turn is attached to a brass rod, which is cemented inside a glass tube M. This glass tube is cemented inside a brass tube D. The complete details are not shown in the diagram, but the adjustment parallel to the axis is secured by means of the ring screw Q. It will be noted that this electrode is insulated from the bronze cylinder. It is of course necessary for the final adjustment that E be capable of movement in a direction parallel to the lines of force, and this is secured by means of a slotted strip of brass attached at right angles to the brass rod, and the electrode holder H_1 is clamped to this strip.

The electrode K_2 is not insulated and consists of a brass rod O which passes through the central boring shown in the cone K_2. The fitting is made air-tight by means of the thick walled rubber tube S. In order to guard against side play in the central brass rod, the bracket W is attached as shown, the final lateral adjustments being effected by means of the screws U_1 and U_2. The rotation of the electrode is secured by a pulley wheel and a belt attached to an electric motor, the velocity being 5 to 10 revolutions a second. At the end of the brass rod is attached the electrode holder H_2 which is slotted and carries a set screw. In the slot is held a strip of tungsten Z, which is ground to the required shape. As the rod is rotated this strip makes and breaks contact with the electrode E, an intermittent arc being thereby formed.

Before use, the lamp is thoroughly exhausted, and then filled with hydrogen, after which the pressure is again reduced to 8 to 10 mm. The residual hydrogen serves to guard against any oxide formation and the presence of oxide bands in the spectrum. A thin strip of mica is introduced between the pole piece P_1 and the electrode E.

In their book Landé and Back [1] give a few details as regards the

[1] *Zeemaneffekt und Multipletstruktur der Spektrallinien*, p. 128, Julius Springer, Berlin, 1925.

preparation of the electrode E about which no general rules can be laid down. Metals of low melting-point, *e.g.* sodium, thallium, lead, etc., can be cast into a copper tube in which a hole is drilled exactly in the axis of the magnetic field opposite to the tungsten striker Z. Metals like chromium and manganese must be powdered and then pressed, whilst metals intermediate between the two extremes, such as bismuth, may be cast in a thin layer on a strip of manganin sheet. Again, the carbon electrodes, coated with the silver alloy in the manner previously described, may be used. The apparatus may also be used for gases, in which case the lamp is filled with the required gas, and purified gas carbon is used for the electrode.

Direct current is employed at 50 to 200 volts, with 1·5 to 3 amperes. The introduction of self-induction improves the sharpness of the spectrum lines and renders the arc more constant.

In his paper on the Zeeman effect with neon Back [1] describes the use of this lamp for exciting this gas. The two cones, K_1 and K_2, are replaced by two glass tubes which are hermetically cemented in. Each of these glass tubes carries a brass rod cemented in and these rods carry at their lower ends thin circular copper discs which are of the same diameter as the flat ends of the pole pieces. These discs are adjusted in the centre of the field so that they are parallel to one another and at right angles to the force lines, the electrode K_2 being no longer rotated. The pole pieces are insulated from the copper discs by the interposition of mica sheets. The discharge is obtained by means of a high potential transformer without a condenser and air-gap, and the pressure of the gas is maintained at 2 to 3 cm. The same arrangement may be used with other gases, in which case the pressure giving the best results varies with the particular gas dealt with. With the discharge through a gas no standard lines are given for use in determination of the field strength. The construction of the apparatus allows a rapid change from one set of electrodes to another without altering the magnetic field. Not only does this enable the electrode E to be renewed during an exposure, but also it permits the arc discharge to replace the gas discharge and so impress the necessary standard lines on the photographic plate. Back says that if the various electrodes in their respective holders have previously been adjusted, the change can be effected in less than two minutes.

A few remarks may be added with respect to the spectrograph that is best suited for the study of the Zeeman effect. In order to analyse the fine structure of a Zeeman pattern the first question which arises is the resolving power. It is a simple matter to calculate the minimum resolving power which is necessary for the measurement of the Zeeman pattern given by any line of a known combination from Landé's table of g values if the strength of the field is known. It will be seen on reference to p. 342 that the separation of any pair

[1] *Ann. der Phys.*, **76**, 317 (1925).

of consecutive components in a Zeeman pattern in terms of the normal triplet separation has a minimum value of $g_x - g_y$, where g_x and g_y are the g-values of the two terms which combine to give the parent line. The wave-number interval, therefore, between the lines which have to be resolved is $(g_x - g_y)\Delta\nu_{\text{norm}}$ or $(g_x - g_y) \times \text{H} \times 4{\cdot}7 \times 10^{-5}$, and the wave-length interval $\Delta\lambda$ is $(g_x - g_y) \times \text{H} \times 4{\cdot}7 \times 10^{-5} \times \lambda^2$. The resolving power necessary to separate the two components is $\lambda/\Delta\lambda$ [1] and we therefore have

$$\frac{\lambda}{\Delta\lambda} = \frac{1}{(g_x - g_y) \times \text{H} \times 4{\cdot}7 \times 10^{-5} \times \lambda}.$$

As an instance we may take the manganese line at $\lambda = 4033$ A, or $4{\cdot}033 \times 10^{-5}$ cm., which was measured by Back,[2] and put $\text{H} = 3 \times 10^4$ Gauss. This line is due to the combination $n^6_{13} - n^6_{23}$, the values of g_x and g_y being 2 and $\frac{6}{35}$, respectively. We have

$$\frac{\lambda}{\Delta\lambda} = \frac{35}{4 \times 4{\cdot}7 \times 10^{-5} \times 3 \times 10^4 \times 4{\cdot}033 \times 10^{-5}}.$$
$$= 154000.$$

It must be remembered that this is the minimum value of the resolving power necessary under perfect conditions of definition, etc. In actual practice a greater value will in all probability be required.

It is obvious that in work on the Zeeman effect the greatest resolving power and the strongest magnetic fields are desirable, and when the best form of spectroscope is discussed we have the choice between the concave grating instrument on the one hand and the interferometer type of instrument (echelon grating, Fabry-Perot and Lummer-Gehrcke interferometers) on the other. Whilst the latter have very high resolving power they have certain disadvantages compared with the former. Owing to the necessity for using monochromatic light with an interferometer, only one line can be observed at a time. Then, again, the successive orders are not sufficiently separated to avoid the overlapping of the Zeeman patterns in two consecutive orders. In the description given on pp. 340 and 341 of the various types of Zeeman patterns the intensity distribution was shown to be the most important criterion for the recognition of the type, and the recognition of the type is the first essential in the analysis of the given pattern. The more the patterns in different orders overlap, the more difficult it becomes to disentangle the components and determine their intensity distribution. The great advantage of the concave grating instrument is that on a single photograph the Zeeman patterns of a number of lines in a large spectral region can be secured, together with the patterns given by selected standard lines for the measurement of the field which will of course be the same for all the patterns shown on that photograph. Further, the type can in

[1] See vol. i., p. 65.

[2] See p. 347.

general be recognised by inspection without difficulty. For ordinary work, therefore, there is no doubt that the concave grating is superior to any other form of dispersing instrument, and in order to obtain the best results the largest size of instrument should be used. The theoretical resolving power of a grating is given by mn,[1] where m is the total number of rulings and n is the order of the spectrum. With a grating having 100,000 rulings the resolving power in the second order is 200,000, whereas with a grating ruled at the National Physical laboratory with 14,400 lines to the inch and a 6-inch ruled surface it is 172,800.

On the other hand, for the accurate analysis of a single Zeeman pattern an interferometer may well be used and indeed may be essential. The final conclusion we reach is that the interferometer with its very large resolving power is of great value in special cases and that for ordinary work the concave grating has material advantages.

Some interesting results have been described by Kapitza and Skinner, who have succeeded in producing very intense magnetic fields and in examining the Zeeman effect with a quartz spectrograph. The method of producing their fields is given in detail by Kapitza [2] and consists in the discharge of a very heavy current through a solenoid for a fraction of a second, excessive heating being thereby avoided. The construction of the apparatus involved four separate problems, namely, the source of energy, the switches and connections, the measurement of the current by means of oscillographs, and the construction of the most efficient type of coils for producing the field.

As the source of power four accumulator batteries of very simple design were constructed. Each battery consisted of 71 lead plates separated by 1·7 mm., the interspace being filled with 30 per cent. sulphuric acid. The four batteries were charged in parallel and for discharging they were connected in two groups of two batteries, and the two groups were connected in series. When the whole is discharged through an external resistance of 0·02 ohm, a power of 1000 kilowatts can be obtained, the current in the most efficient discharge being about 7000 amperes.

A system of specially constructed switches is employed for making the circuit, the breaking being effected by the burning of a copper fuse wire which is thrown into the circuit at a definite interval after the circuit has been completed. It was found that this method is by far the best for effecting a sudden interruption in the current.

Some preliminary observations of the Zeeman effect observed with the use of these intense fields have been given by Kapitza and Skinner.[3] The period during which the field lasts is of the order of 1/100th second and the source of light is a single spark, produced by a large high-tension battery. The single spark is of sufficient intensity with the use of a quartz spectrograph, and the resolving power of this

[1] See vol. i., p. 152.

[2] *Proc. Roy. Soc.*, A. **105**, 691 (1924).

[3] *Nature*, **114**, 273 (1924).

instrument is large enough with the fields of 130,000 Gauss which were employed. The spark takes place in a coil of 5 mm. internal diameter in which the field is produced, and the spark and field are timed to occur simultaneously. The observations were made along the lines of force and in general it was found that the resolution was the same as that obtained in smaller fields. Some interesting cases of the Paschen-Back effect were noted, and in particular the case of the six membered *pp** group of beryllium may be mentioned, which as a whole showed the normal triplet. Some interesting cases of lines appearing in the field and not in its absence were observed, as well as some lines which disappeared in the field. The lines are shifted by varying amounts towards the red by the field, but this may probably be due to a kind of pressure effect owing to the production of the spark in the field.

We may next turn our attention to the measurement of the photographs of the Zeeman patterns, and first consider the determination of the strength of the field from the separation of the standard lines which have been included for this purpose, as already explained. For this purpose any lines may be used, the Zeeman patterns of which are definitely known. For example, the use of the two aluminium lines at $\lambda = 3944$ and 3961, giving the D_1 and D_2 types, has already been mentioned. Landé and Back [1] say that the most suitable lines for use as standards are those which have a greater wave-length than $\lambda = 4000$, show more than three components with wide separations, and are given by combinations between terms of small azimuthal quantum numbers. The last criterion ensures the use of lines with maximum sharpness of definition, whilst the others ensure greater accuracy of measurement of the components. They recommend the use of the sharp triplets of zinc and cadmium given in Table CLXXXVII.

TABLE CLXXXVII.

Zn.	Cd.	Combination.	g_x.	g_y.	Zeeman pattern.
4810·71	5086·06	$n^3_{22} - n^3_{11}$	$\frac{3}{2}$	2	$\frac{\pm (0)\ (1)\ 2\ 3\ 4}{2}$
4722·34	4800·09	$n^3_{21} - n^3_{11}$	$\frac{3}{2}$	2	$\frac{\pm (1)\ 3\ 4}{2}$
4680·38	4678·37	$n^3_{20} - n^3_{11}$	$\frac{0}{0}$	2	$\frac{\pm (0)\ 4}{2}$

Since all these lines give anomalous resolution the measurements will be affected to a certain extent, depending on the strength of the field, by distortion. This phenomenon will be discussed in detail subsequently, and all that it is necessary to say here is that the determination of the field strength should be made for each of the chosen standards separately and the mean taken of the values thus found. In this way the danger of errors arising from the distortion is reduced to a minimum.

[1] *Loc. cit.*, p. 135.

In order to calculate the field strength it is obvious that the value of $\Delta\nu_{\text{norm}}$ be known, and this may be taken as $4{\cdot}7 \times 10^{-5}$ cm. $\times$ H without any serious error being introduced. It may be pointed out that in ordinary work the measurements of Zeeman patterns are made relatively to those of the standard lines.

There now remain to be considered the sources of error in the analysis of Zeeman patterns. There is first the danger of inaccurate measurement, and this can be minimised in the usual way by taking the mean of several measurements, the probable error of such means depending on the sharpness of the resolution of the Zeeman pattern. It will be found, however, that all anomalous patterns exhibit a definite distortion or asymmetry, that is to say, the Zeeman type is an ideal pattern to which the observed pattern more or less approximates. This distortion increases with the strength of the field and depends on the mutual influence of two or more lines of a doublet, triplet, etc. (incipient Paschen-Back effect). The distortion therefore increases the nearer the component lines of a series member lie together and it also increases with the strength of the field. We are indebted to Back for demonstrating how this distortion makes its appearance and also for the method of correcting it. When the lines of a group are far apart the distortion is negligible, as may be seen from the diffuse doublet of thallium at $\lambda = 3519{\cdot}230$, $3529{\cdot}400$, and $2767{\cdot}870$. Back's measurements[1] of the first two lines are given in Tables CLXXXVIII and CLXXXIX.

TABLE CLXXXVIII.

Tl $\lambda = 3519{\cdot}230$, H = 39110 Gauss.

Component.	Polarisation.	Intensity.	Wave-length.	$\Delta\lambda$.
12	s	1	3519·545	
				0·029
11	s	3	3519·516	
				0·030
10	s	7	3519·486	
				0·031
9	s	9	3519·455	
				0·181 = 6 × 0·0302
8	p	10	3519·274	
				0·030
7	p	10	3519·244	
				0·030
6	p	10	3519·214	
				0·031
5	p	10	3519·183	
				0·178 = 6 × 0·0297
4	s	9	3519·005	
				0·030
3	s	7	3518·975	
				0·031
2	s	3	3518·944	
				0·031
	s	1	3518·913	

[1] *Ann. der Phys.*, **70**, 333 (1923).

The complete symmetry of the pattern recorded in Table CLXXXVIII. is shown in two ways. Not only is the separation of the components of like polarisation constant (0·030), but also the means of each pair of corresponding components is exactly equal to the wave-length of the parent line.

In order to analyse the pattern, we first of all calculate $\Delta\nu_{\text{norm}}$ which is given by

$$\Delta\nu_{\text{norm}} = 4{\cdot}7 \times 10^{-5} \times 39110$$
$$= 1{\cdot}838,$$

and expressed in wave-lengths this becomes $1{\cdot}838 \times (3{\cdot}51923 \times 10^{-5})^2$ or 0·2277 A. The measured separation of $\Delta\lambda = 0{\cdot}030$ A., expressed as a fraction of the normal interval, is 0·1318, which is very nearly $\frac{2}{15}$ ($\frac{2}{15} = 0{\cdot}1333$), the difference being about 1 per cent. The Zeeman pattern, therefore, is given by

$$\frac{\pm(1)\ (3)\ 15\ 17\ 19\ 21}{15},$$

and this, as shown on p. 326, is that given by the combination $n_{22}^2 - n_{33}^2$ or $p_1 d_1$ on the old system of notation, the values of g being $\frac{4}{3}$ and $\frac{6}{5}$ respectively.

TABLE CLXXXIX.

Tl λ = 3529·400, H = 39110 Gauss.

Component.	Polarisation.	Intensity.	Wave-length.	$\Delta\lambda$.
10	s	9	3529·767	
				0·125 = 2 × 0·0625
9	s	8	3529·642	
				0·059
8	p	10	3529·583	
				0·062
7	s	8	3529·521	
				0·059
6	p	2	3529·462	
				0·124 = 2 × 0·062
5	p	2	3529·338	
				0·060
4	s	8	3529·278	
				0·061
3	p	10	3529·217	
				0·060
2	s	8	3529·157	
				0·062
1	s	9	3529·035	

In Table CLXXXIX. the complete symmetry is again shown in the same two ways as in the previous table. The mean value of the minimum separation of the components is 0·061165 and the normal triplet interval expressed in wave-lengths is now $1{\cdot}838 \times (3{\cdot}5294 \times 10^{-5})^2$ = 0·229 A. The measured interval $\Delta\lambda = 0{\cdot}061165$, expressed as a

fraction of the normal interval, is 0·2671, which is almost exactly $\frac{4}{15}$ ($\frac{4}{15} = 0{\cdot}2667$). The Zeeman pattern, therefore, is expressed by

$$\frac{\pm (4)\ 8\ (12)\ 16\ 24}{15}$$

and this is given by the combination $n_{22}^2 - n_{32}^2$ or $p_1 d_2$, the values of g being $\frac{4}{3}$ and $\frac{6}{5}$, respectively.

Unfortunately the Zeeman pattern of the third line of the diffuse doublet could not be analysed owing to the complex structure of the parent line, but the reality of the symmetry of the magnetic resolution is sufficiently established by the measurements given above.

The wave-number interval between the above two thallium lines is $\Delta\nu = 82$ and this is sufficiently large to prevent any mutual distortion of their Zeeman patterns in fields of 39110 Gauss. Turning now to the corresponding copper diffuse doublet, $\lambda = 5218{\cdot}200$, 5220·080, and 5153·260, the first two lines are separated by $\Delta\nu = 6{\cdot}6$ only, and the Zeeman patterns of both are very seriously distorted. Back's measurements [1] are given in Table CXC.

The distortion of these two Zeeman patterns is obvious from an inspection of the observed wave-lengths. In the case of the first line the separations of consecutive components varies from 0·029 to 0·085, and in the second line they vary from 0·114 to 0·189. As these measurements stand it is impossible to calculate the g values of the combining terms and hence determine the series to which the lines belong. In spite, however, of the great distortion it is possible to recognise the fundamental type of each pattern, which is clearly Type 4 in the case of $\lambda = 5218$ and Type 6 in the case of $\lambda = 5220$, that is to say the lines belong to a system of even multiplicity. The absence of a zero p-component shows that the system is not uneven.

As a matter of fact Back shows that, provided the distortion is not so great as to render the recognition of the fundamental type impossible, the distortion may be corrected in a very simple manner. He shows that the mean of all of the separations of the components of like polarisation is very near to the theoretical value. This may be first demonstrated from the 5218 line. The mean of the separations of the s-components is 0·0585, if we neglect the value 0·029, because the corresponding interval between components 1 and 2 was not measured. The mean of the separations of the p-components is 0·0647 and the mean of the whole is 0·0616.

Now the value of $\Delta\nu_{\text{norm}}$ for this line is $4{\cdot}7 \times 10^{-5} \times 37010$ and in terms of wave-length it is

$$\Delta\lambda = 4{\cdot}7 \times 10^{-5} \times 37010 \times (5{\cdot}2182 \times 10^{-5})^2 = 0{\cdot}4737.$$

[1] *Loc. cit*

TABLE CXC.

Cu $\lambda = 5218{\cdot}200$, H = 37010 Gauss.

Component.	Polarisation.	Int.	Wave-length, obs.	Δλ.	Wave-length, calc.	Δλ.
12	*s*	1	5218·764		5218·863	
				0·029		0·063
11	*s*	8	5218·735		5218·800	
				0·031		0·063
10	*s*	8	5218·704		5218·737	
				0·034		0·064
9	*s*	8	5218·670		5218·673	
				0·391		0·378
8	*p*	7	5218·279		5218·295	
				0·074		0·063
7	*p*	10	5218·205		5218·232	
				0·068		0·064
6	*p*	10	5218·137		5218·168	
				0·052		0·063
5	*p*	7	5218·085		5218·105	
				0·356		0·378
4	*s*	8	5217·729		5217·727	
				0·085		0·064
3	*s*	4	5217·644		5217·663	
				0·084		0·063
2	*s*	1	5217·560		5217·600	
						0·063
1	*s*	—	—		5217·537	

Cu $\lambda = 5220{\cdot}08$, H = 37010 Gauss.

10	*s*	2	5220·857		5220·837	
				0·257		0·252
9	*s*	4	5220·600		5220·585	
				0·167		0·126
8	*p*	8	5220·433		5220·459	
				0·151		0·127
7	*s*	4	5220·282		5220·332	
				0·134		0·126
6	*p*	1	5220·148		5220·206	
				0·189		0·252
5	*p*	1	5219·959		5219·954	
				0·114		0·126
4	*s*	4	5219·845		5219·828	
				0·118		0·127
3	*p*	10	5219·727		5219·701	
				0·119		0·126
2	*s*	4	5219·608		5219·575	
				0·241		0·252
1	*s*	3	5219·367		5219·323	

Expressed as a fraction of this normal interval the separation 0·0616 becomes 0·1301. This is very near to 0·1333 or $\frac{2}{15}$, which is the value of $g_x - g_y$, *i.e.* $\frac{4}{3} - \frac{6}{5}$ for the $n^2_{22} - n^2_{32}$ or $p_1 d_1$ line of a doublet system. Assuming that the value 0·1333 is correct, the wave-length separation of consecutive components of like polarisation in a field of 37010 Gauss becomes 0·06315. By the use of this value and the known pattern

$$\frac{\pm (1)\ (3)\ 15\ 17\ 19\ 21}{15},$$

the wave-lengths in the sixth column of the upper part of Table CXC. were calculated. It will be noticed that the effect of the distortion is apparently to displace the whole pattern towards the blue with the exception of the two strongest *s*-components (4 and 10) which are very close to their calculated positions.

An exactly similar calculation may be made with the 5220 line. The mean of the separations of the *s*-components is 0·263 and in the case of the *p*-components it is 0·235. The grand mean is 0·249. Expressed as a fraction of the normal wave-length separation (0·474) this becomes 0·5258 which is very nearly 0·5333 or $\frac{8}{15}$. This is the value of $g_x - g_y$ for the $p_1 d_2$ combination in a doublet system, and from this the values given in the sixth column of the lower half of Table CXC. have been calculated.

The case of the third line of the doublet, $\lambda = 5153{\cdot}26$, is very interesting, since it shows distortion in spite of the fact that it is widely separated from the other two lines. Back attributes this to the influence of the fourth line which is normally forbidden by the selection principle. The forbidden $p_2 d_1$ transition may, however, take place in the presence of an external field and, though he was unable to observe it on his photographs, Back assumes that it is real enough to influence the 5153 line in the magnetic field. The calculated wave-length of this forbidden line is 5151·46. The measurements of the Zeeman pattern given by the 5153 line are set forth in Table CXCI.

TABLE CXCI.

Cu $\lambda = 5153{\cdot}26$, H = 37010.

Component.	Polarisation.	Int.	Wave-length.	Δλ.	Wave-length.	Δλ.	
6	*s*	7	5153·652		5153·660	0·062	0·369
				0·360			
5	—	—	—		5153·598	0·307	
4	*p*	10	5153·292		5153·291		
				0·064		0·062	
3	*p*	10	5153·228		5153·229		
				0·319		0·307	
2	*s*	4	5152·909		5152·922		
				0·059		0·062	
1	*s*	9	5152·850		5152·860		

In the absence of component 5 it is only possible to determine the separation by taking the mean of 0·064 and 0·059, which is 0·0615. The value of the normal interval expressed in wave-lengths at $\lambda = 5153$ is

$$\Delta\lambda = 4{\cdot}7 \times 10^{-5} \times 37010 \times (5{\cdot}15326 \times 10^{-5})^2$$
$$= 0{\cdot}4619 \text{ A.},$$

and the separation expressed as a decimal fraction of this normal interval is 0·1331, which is almost exactly 0·1333 or $\frac{2}{15}$. Using

this value, the true separation is found to be 0·0616 and the wavelengths in the sixth column of Table CXCI. have been thus calculated. The Zeeman pattern, therefore, is found to be

$$\pm \underset{15}{(1)\ 11\ 13}.$$

Attention may be drawn to the fact that the intensity distribution is also affected to a certain extent when distortion is present. This may at once be seen from the observed intensities given in the third column of Tables CXC. and CXCI. In spite of this, however, it is possible in each of the three patterns to recognise the fundamental type, since it is easy to determine whether the intensities of the components increase or decrease from the centre outwards. This is the criterion by means of which the fundamental type is identified, and, as already stated, Back has shown that the distortion can be corrected, provided that it is not sufficiently great to render the fundamental type unrecognisable.

In conclusion, it may be pointed out that the whole basis of Back's method of correcting the effects of distortion rests on the validity of Landé's g-formula and on the permanence of the g-sums. The latter law is entailed in that the sums of the separations of the components are taken and the mean value of the separation found therefrom. Both the g-formula and the law of permanence of g-sums have been placed on so sure a footing by independent experimental observation that complete confidence may be placed in this method of correcting the effects of distortion due to the incipient Paschen-Back effect.

CHAPTER III.

THE STARK EFFECT.

A VERY interesting and important phenomenon was discovered by Professor J. Stark in 1914. He found that under the influence of an electric field the lines of the Balmer series of hydrogen are resolved into components when the emission takes place in an electric field. It was soon found that the phenomenon is by no means peculiar to hydrogen and it is generally known as the Stark effect. It is only right to point out that an observation of the phenomenon was independently made by Lo Surdo at a date which he said preceded Stark's observation.

Lo Surdo endeavoured to study the Doppler effect due to retrograde canal rays near to the cathode, with a discharge tube placed perpendicularly or obliquely to the slit of a spectroscope. He then noted that the hydrogen lines were resolved into several components and found, as Stark also discovered, that the components were polarised, partly parallel and partly perpendicular to the direction of the field.

Whilst the so-called canal rays were discovered by Goldstein, Stark made an exhaustive investigation into their nature, and he recognised the possibility of using them in order to determine whether a phenomenon analogous to the Zeeman effect existed in an electric field. As will be shown below, Stark's method of experimentation consists in the application of a known electric field to a layer of rarefied gas caused to luminesce by means of canal rays. In this way he was able to correlate the separation of the components with the strength of the field, a relation which is of fundamental importance.

Lo Surdo, on the other hand, investigated the radiations emitted by the gas molecules in the Crookes dark space between the cathode and the negative glow. Owing to the steep potential gradient in this region the emission takes place in an electric field and the Stark effect is easily observed. In the first place, the resolution is not constant and naturally decreases the greater the distance from the cathode, and in the second place there is no direct method of measurement of the electric field at any point. From an experimental point of view the Lo Surdo method is by far the simplest, but the observations must necessarily have remained qualitative had not Stark by his method obtained quantitative measurements. Stark's measurements of the relation between separation and strength of field enable the Lo Surdo method to be made quantitative, since his values for the

hydrogen lines may be used to determine the strength of the field at any point in the cathode dark space. In short, it may be said that although Lo Surdo carried out a considerable amount of work in the study of this phenomenon, it is to Stark that we are indebted for the accurate investigation of the resolution of the hydrogen lines which established the quantitative relationship between the separation of the components and the strength of the field. A list of the papers published by Lo Surdo [1] and by Stark [2] and his co-workers is given at foot of this page, and in dealing with their work no further reference to these need be made.

In view of the fundamental importance of the quantitative results obtained with hydrogen it will be preferable first to describe in some detail Stark's quantitative measurements by his canal ray method, and then to discuss the observations made with helium and some metals. In so doing we shall to a certain extent not follow a chronological sequence of the advances as these were made, but will gain in obtaining a clearer understanding of the phenomenon. It may also be pointed out that from the theoretical point of view this method possesses an advantage, since the theory, like that of spectral series, has only succeeded at present in offering a quantitative explanation of the phenomena so far as atoms of the hydrogen type are concerned.

It will be convenient at the outset very briefly to indicate the essential facts which have been observed, the most important being that when the hydrogen lines are emitted in an electric field they no longer appear single but are resolved into a number of components. The number and distribution of these components depend on the direction of the observation, that is to say, whether the collimating axis of the spectroscope is parallel or perpendicular to the lines of force of the electric field. Further, when the observations are made across the lines of force (the transverse effect) the lines are linearly polarised, partly parallel to and partly perpendicular to the lines of force. It must be understood that this definition of polarisation refers to the direction of the electric vibration in the light ray, and that the electric vibration in the case of some components is parallel to and in others perpendicular to the lines of force of the electric field. This is just the opposite to the position of the plane of polarisation as determined by a Nicol prism, since the plane of polarisation is perpendicular to the direction of the electric vibration in the light ray.

It might at first sight seem that the Stark phenomenon is analogous

[1] Lo Surdo, *Atti R. Acad. Lincei*, **22**, ii. 664 (1913); **23**, i. 82, 113, 143, 252, 326 (1914); *Phys. Zeitsch.*, **15**, 122 (1914).

[2] J. Stark, *Berliner Ber.*, **40**, 932 (1913); *Ann. der Phys.*, **43**, 965 (1914); J. Stark and G. Wendt, *ibid.*, **43**, 983 (1914); J. Stark and H. Kirschbaum, *ibid.*, **43**, 991, 1017 (1914); J. Stark, *ibid.*, **48**, 193, 210 (1915); J. Stark, O. Hardtke and G. Liebert, *ibid.*, **56**, 569 (1918); J. Stark, *ibid.*, **56**, 577 (1918); G. Liebert, *ibid.*, **56**, 589, 610 (1918); J. Stark and O. Hardtke, *ibid.*, **58**, 712 (1919); J. Stark, *ibid.*, **58**, 723 (1919); J. Stark, *Elektrische Spektralanalyse chemischer Atome*, Hirzel, Leipzig, 1914.

to the Zeeman effect, but in actual fact they are very different. In the first place, with a given magnetic field the number of components observed in the Zeeman effect and their distribution with respect to the undisturbed line are constant for all the lines of a given spectral series and indeed for the same series type with different elements. In the Stark effect, with a given electric field, the number of components increases within a single series as the order number of the line increases, and, furthermore, the separation between the components increases. In the second place, an essential difference between the two phenomena is to be found in the fact that in the Zeeman effect the components observed when the observation is made along the lines of force (the longitudinal effect) are circularly polarised, whilst in the Stark effect, at any rate in the case of hydrogen, the components are not polarised.

The Stark effect, apart from its experimental interest, has a great significance from a theoretical standpoint. The application of the energy quantum theory to the phenomena of spectral series and the Zeeman effect has already been discussed in the preceding two chapters and the remarkable advance that has resulted in our knowledge of atomic phenomena will be surely manifest to all who study the work of Bohr and his co-workers, and of Sommerfeld and the German physicists. The application of the quantum theory to the Stark effect and the remarkably neat explanation thereby found of the quantitative observations may indeed be considered as one of the most striking achievements of this theory. If it were possible that anyone still doubts the justification of the fundamental assumptions of this theory, let such a one consider the Epstein explanation of Stark's results, and then surely doubt must give place to a glad recognition of a more than notable advance in physical concepts, which must lead to a still greater understanding of the structure of the atom.

We may first consider the design of the discharge tubes which Stark used in his investigations with hydrogen. In the rarefied gas two plane electrodes are mounted close together so that a great potential difference between them cannot induce any form of discharge. The distance between the two discs must not exceed 3 mm. when the pressure of the gas is such that the cathode dark space extends over several centimetres. These electrodes must not touch the walls of the discharge tube and at the same time they must be so close to the walls that no discharge can find its way between. These two electrodes form the positive and negative poles of the electric field and the luminescence of the gas in the space between them is produced by means of canal rays.

Two different designs of discharge tubes are required, one for observations across the lines of force, and the other for observations along the lines of force. For the former, that is to say the transverse effect, the design of the apparatus is shown in Fig. 40. Two electrodes, F and K, are mounted close together in a glass tube which is 3·6 cm.

in diameter. F is a plane disc of aluminium, 2-3 mm. thick, which is sealed in position as indicated in the diagram. K is a second aluminium disc 2 mm. thick which is riveted on to the end of an aluminium ring about 2 cm. long. This ring is supported by a stout aluminium wire which is attached to a platinum wire sealed on at the end of the side tube in the usual way. The flat disc K is drilled with a number of circular holes 1 mm. in diameter.

At the further end of the discharge tube is mounted a third plane electrode A at a distance of 10-15 cm. from K. A high potential direct discharge is passed between A and K, the latter being the cathode. The pressure of the gas is so adjusted that there is a potential fall of 3000-10,000 volts in front of the cathode. This potential gradient causes the acceleration of the canal rays towards the cathode and they pass through the holes in K with the result that luminescence is visible in the space between F and K. By some convenient means a potential difference is set up between F and K, and this causes a

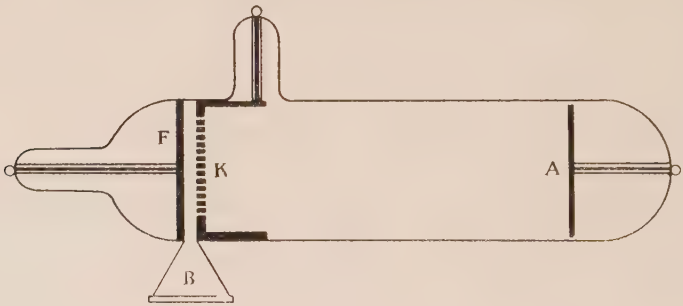


FIG. 40.

discharge between them, provided that ionisation is set up by the canal rays. The potential difference between F and K may be measured by means of an electrometer and, if it is uniform, the strength of the field is given by

$$F = \frac{V}{a},$$

where V is the potential difference and a is the distance in cms. between the plates. In order to guard against too strong a discharge between these two, a resistance is placed in the circuit, which must be adjusted so that the potential difference does not exceed $\frac{1}{10}$th to $\frac{1}{5}$th of that between the two electrodes A and K. The discharge between F and K under the right conditions amounts to from 1 to 10 milliamperes. The observations may be made through a quartz or fluorite window cemented on to the conical side tube B.

In order to observe the longitudinal effect a different form of discharge tube must be used, and a convenient design for the obser-

vation of this effect with gases such as hydrogen or helium is shown in section in Fig. 41. The cathode K of the main discharge is constructed in the same way as in the previous case, but the aluminium disc has only cut in it one rectangular hole 3 × 1·5 mm., through which the canal rays pass. Riveted on to the back of K is a circular aluminium plate F, drilled with 1 mm. holes, and consequently the canal rays follow a course which is parallel to the surface of F, which forms one pole of the electric field. The other pole of this field is the aluminium disc B, 8 mm. in diameter, which is mounted parallel to F. Surrounding B is a glass tube which is ground flat at its end and so mounted that it touches the disc F. In the side of this glass tube a hole 3×1·5 mm. is cut, this hole being immediately under the corresponding hole in the electrode K. This allows the canal rays to pass without hindrance into the electric field between F and B. Care must be taken that the glass tube does not touch either the disc B or the disc K,

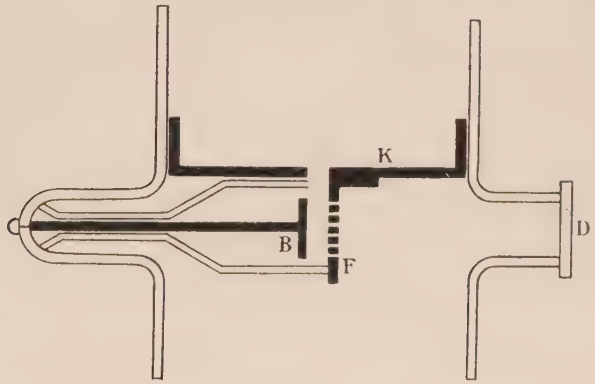


FIG. 41.

and that there is a clearance in each case of 0·5 to 0·75 mm. The observations are made through the quartz or fluorite window D.

The choice of spectrograph for the examination of the resolved lines is a matter of some importance. In the case of the Zeeman effect the resolution picture obtained with a given magnetic field is the same for all spectrum lines of the same series type, but the phenomenon is very different in the Stark effect. In the first place, the number of components varies with the order number of the line in one series of any one element, and in the second place with a given field the separations between the various components are multiples of a constant value measured in wave-numbers or frequencies. The resolution picture, therefore, will vary in magnitude with the various lines in a given series, increasing towards the ultra-violet.

The first mentioned phenomenon is important from the observational point of view because an increase in the number of components

means a decrease in their intensity, since the intensity of the original line is distributed amongst the components. Then again, as is well known, the intensity of the lines decreases as the order number rises, so that the problem of the intensity of the Stark components becomes a serious one in the higher members of a series. The essential condition to be aimed at is the optimum light efficiency combined with a high resolving power. The variation in size of the resolution picture is also a point to be considered in connection with the dispersion of the instrument. Stark describes in some detail the various spectrographs used by him at various stages of the development of his work, but it is not necessary to enter into these. Suffice it to say that he used both a prism spectrograph and a plane grating instrument, a concave grating not being advisable owing to the loss of intensity caused by the astigmatism. There is no need to emphasise the importance of using the instrument to the best advantage, that is to say of avoiding loss of light by the lenses not being fully illuminated.

The next point which concerns us is the polarisation of the components of the resolution picture, and in the transverse effect they are polarised partly parallel and partly perpendicular to the lines of force of the electric field. In order to separate the *p*- and *s*-components and to determine their polarisation a calcite rhomb or a Wollaston prism may be used. By means of an objective lens an image of the light is focussed on to the spectrograph slit, and the rhomb or prism is set up between the light and the lens. Two images are thus obtained on the slit, and the doubly refracting apparatus is so adjusted that the electric vibrations in one image are parallel and in the other are perpendicular to the force lines of the field. One half of the resulting spectrum photograph will include all the *p*-components and the other half will include all the *s*-components, whilst those components which are unpolarised or partially polarised will be present in both halves of the photograph.

It will be remembered that in the Zeeman phenomenon the components are circularly polarised when the observations are made along the lines of force. In the Stark effect with hydrogen it was proved by the use of a suitable quarter-wave plate that there is no circular polarisation, the components observed in the longitudinal effect being unpolarised.

Before dealing with the quantitative observations made by Stark with hydrogen in the strongest fields, we may review some of the results obtained by him in weaker fields, that is to say, fields not greater than 40,000 volts per cm. These results refer only to the strongest components. In the upper portion of Fig. 42 is shown a diagrammatic representation of the components observed with the line H_γ in an electric field of less than 40,000 volts per cm. In the transverse effect there are four *p*-components, the two outer ones having a much greater intensity than the two inner ones. There are three *s*-components of equal intensity. In the longitudinal effect three unpolarised components are obtained which have the same

wave-lengths as the *s*-components in the transverse effect. In the lower part of Fig. 42 is shown the Zeeman effect as obtained with the same line, namely, the normal triplet, and it is important to notice the great difference in magnitude between the two effects; whereas the difference between the outer components in the Zeeman effect with a magnetic field of 30,000 Gauss is about 0·5 A., the distance between the outer components in the Stark effect with an electric field of 30,000 volts per cm. is about 13 A.

In the case of the Stark effect with hydrogen the distance between the components is directly proportional to the strength of the electric field. If the separation between the outer components is plotted against the field strength a straight line is obtained which passes through the origin $F = 0$, $\Delta\lambda = 0$. The slope of this line

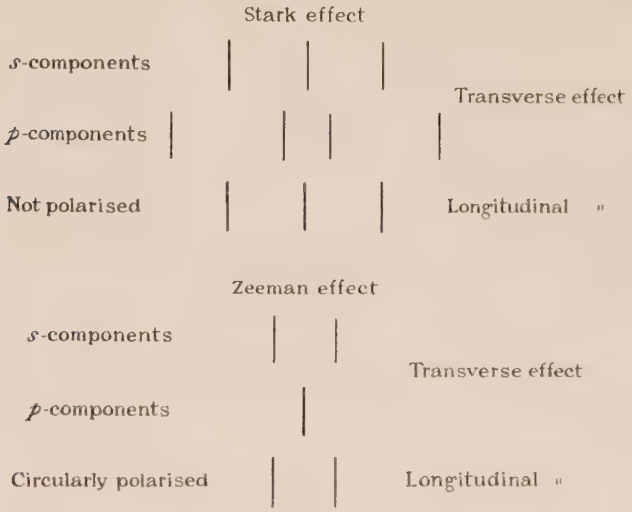


FIG. 42.

for the Balmer series is different for the *p*- and the *s*-components and it increases as the order number of the line in the series increases. In Fig. 43 are shown the results obtained with the two lines H_β and H_γ.

The establishment of this law is of great importance since the values obtained by Stark can be used to measure the strength of the field in Lo Surdo's method of observation, when the hydrogen lines are present in the spectrum. As will be shown later this law does not hold in the case of other elements except with a few of the helium lines.

In his earlier work with small fields Stark was able to establish the fact that the number of components obtained by the resolution of the hydrogen lines increases with the order number of the lines,

even though he was only observing the stronger components. He gives a table of these components observed with the first four hydrogen lines in a field of 28,500 volts $\times$ cm.$^{-1}$ together with their separations from the position of the undisturbed line. Since the measurements are not as accurate as those obtained in subsequent work they need not be quoted here, but the increase in the number of the components observed in the transverse effect is shown in Table CXCII.

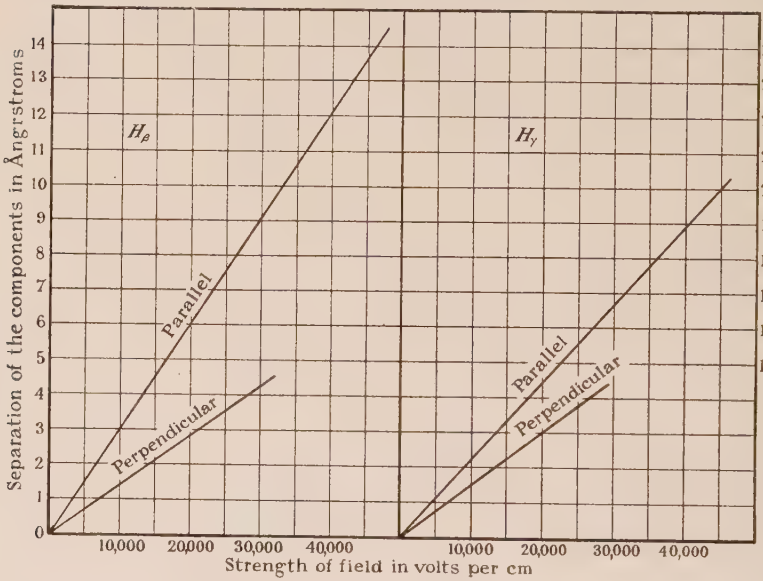


FIG. 43.

TABLE CXCII.

	p-components.	*s*-components.	Total.
H_α	2	1	3
H_β	3	3	6
H_γ	4	3	7
H_δ	4	4	8

Stark also noticed a remarkable variation in the relative intensities of the components according to the direction of the field in relation to the direction of travel of the canal ray stream.

This phenomenon will be dealt with below in connection with Stark's latest work on the fine structure of the resolution picture of the hydrogen lines obtained in very strong fields.

The next point to be referred to is the symmetry of the resolution obtained with the hydrogen lines. This symmetry is perfect as re-

gards the distribution of the components, there always being the same number of components on each side of the undisturbed line, and the separation of each corresponding pair of components is exactly the same with respect to the undisturbed line.[1]

We may now turn to Stark's final work on the hydrogen lines which was published in 1915. In order to study the complete resolution picture and measure the wave-lengths of all the components it is necessary to make use of very strong fields. In his investigation of the phenomenon exhibited by the first four lines of the Balmer series Stark employed a field of 104,000 volts $\times$ cm.$^{-1}$ and dealt only with the transverse effect. Since the results of his measurements are very important from the theoretical point of view we may describe them in detail.

There are three points which must be mentioned in connection with the experimental method. In the first place, when very strong fields are used there is a tendency for the two discs, which form the two poles of the field (F and K in Fig. 40) to become displaced owing to the strong attraction between them. The distance between these two discs is kept constant by means of four rods of fused quartz placed at the four corners of a square. The method of mounting one of these rods is shown in section in Fig. 44, where the upper disc forms the cathode of the main discharge. The quartz rod slides in a hole drilled in a small metal block which is attached to the lower disc. The adjustment is effected by a brass screw with a broad drum head which presses against the quartz rod.

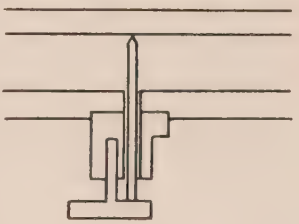


FIG. 44.

In the second place, Stark set up the discharge tube vertically so that the path of the canal rays was parallel to the slit of the spectrograph. There are certain advantages in this arrangement, such for instance as the more symmetrical cooling due to the surrounding air. The particular disadvantage is that the amount of light reaching the spectrograph is small, but this is outweighed by the fact that if the field is not uniform this is shown by a curvature of the components. It follows that a horizontal line drawn through any part of the spectrum photograph corresponds to an equal field strength. Stark found for the examination of the transverse effect, with which we are now particularly concerned, that this is the best arrangement.

In the third place, we have not as yet discussed the polarity of the field with reference to the main discharge. Clearly there are two ways of orienting the electric field, one in which the potential gradient is in the same direction, and the other in which the potential gradient

[1] Later work has shown that this is not strictly true as regards H_γ. See below, pp. 433 and 467.

is in the opposite direction to that of the main discharge. As far as the actual resolution is concerned this is the same in both the two alternative methods, but the relative intensities of corresponding components are different. With the first alternative, or what may be called the direct field, the longer wave components have the greater intensity, whilst with the second alternative, or the opposed field, the shorter wave components have the greater intensity. In view of the fact that this intensity variation has not been especially investigated Stark chose of the two alternatives that one which gave the best results, namely, the second or the opposed field. The reasons for this choice were as follows. In the first place, the opposed field greatly increases the strength of the canal rays and thus also the intensity of the illumination within the field. The anode of the principal discharge becomes heated partly by the cathode rays and partly by the rays which pass back from the field through the holes in the principal cathode. The amount of heating caused by the second effect is less with the opposed field and consequently the canal rays may be made more intense with a resulting greater amount of luminosity in the case of the opposed field.

In the second place, the opposed field gives a greater strength of field and hence a greater resolution of the components than the direct field with equal potential difference and equal resistance in the field circuit. As has already been stated the potential difference always causes an electric discharge across the field, and the stronger this is the greater is the potential drop caused by the auxiliary resistance and hence the weaker is the field. This discharge is very much less with the opposed field than with the direct field. If an induction coil is used for the principal discharge, then for the same reading of the electrometer the resolution is from 10 to 20 per cent. less with the direct field than it is with the opposed field. Further, owing to the greater variations in the field strength, the components observed with the direct field are broader and less sharply defined.

A few words may be added with reference to the statement made above as to the change of intensity of the components when the direction of the field is changed. With a given direction of field any two components with equal separations, that is to say, each pair for which $\Delta\lambda$ is the same, have not the same intensities. The ratio of their intensities is reversed when the direction of the field is reversed. Since the important matter is the intensity distribution amongst all the components, Stark measured the intensities of each corresponding component on the two sides of the undisturbed line with both direct and opposed fields. He gave the mean of the values obtained with the two fields to each pair.

In Table CXCIII. are given the number, distribution, and intensity of the various components observed in the transverse effect with the first four hydrogen lines in a field of 104,000 volts $\times$ cm.$^{-1}$.

TABLE CXCIII.

H_α.

Nature of the components.	Number of component.	Distance from centre in A.	Intensity.	Remarks.
p-components .	3	11·5	1·2	
	2	8·8	1·1	
	+ 1	+ 6·2	1·0	
	− 1	− 6·2	1·0	
	2	8·8	1·1	
	3	11·5	1·2	
s-components . .	+ 1	+ 2·6	1·0	
	0	0	2·6	
	− 1	− 2·6	1·0	

H_β.

p-components .	6	19·4	1·0	Doubtful.
	5	16·4	11·5	
	4	13·2	9·1	
	3	10·0	4·8	
	2	6·7	1·0	
	+ 1	+ 3·3	1·2	
	0	0	1·4	
	− 1	− 3·3	1·2	
	2	6·7	1·0	
	3	10·0	4·8	
	4	13·2	9·1	
	5	16·4	11·5	
	6	19·4	1·0	Doubtful.
s-components . .	6	19·3	1·0	
	5	16·4	1·1	
	4	13·2	1·3	Doubtful.
	3	9·7	9·7	
	2	6·6	12·6	
	+ 1	+ 3·4	3·3	
	0	0	1·4	
	− 1	− 3·4	3·3	
	2	6·6	12·6	
	3	9·7	9·7	
	4	13·2	1·3	Doubtful.
	5	16·4	1·1	
	6	19·3	1·0	

TABLE CXCIII.—*Continued.*

H_γ.

Nature of the components.	Number of component.	Distance from centre in A.	Intensity.	Remarks.
p-components	7	29·4	1	Doubtful.
	6	23·9	10·8	
	5	19·9	7·2	
	4	15·9	2·0	
	3	10·6	1	
	2	6·6	1·5	
	+ 1	+ 2·7	1·6	
	− 1	− 2·7	1·6	
	2	6·6	1·5	
	3	10·6	1	
	4	15·9	2·0	
	5	19·9	7·2	
	6	23·9	10·8	
	7	29·4	1	Doubtful.
s-components	6	26·3	1·1	
	5	22·8	1	
	4	17·3	6·1	
	3	13·3	4·3	
	2	9·7	1·2	
	+ 1	+ 3·9	3·6	
	0	0	7·2	
	− 1	− 3·9	3·6	
	2	9·7	1·2	
	3	13·3	4·3	
	4	17·3	6·1	
	5	22·8	1	
	6	26·3	1·1	

H_δ.

p-components	8	37·5	1	Doubtful.
	7	33·4	7·2	
	6	28·6	2·8	
	5	24·2	1·1	
	4	19·6	1·2	
	3	14·4	1·5	
	2	9·6	1·2	
	+ 1	+ 5·2	1	
	− 1	− 5·2	1	
	2	9·6	1·2	
	3	14·4	1·5	
	4	19·6	1·2	
	5	24·2	1·1	
	6	28·6	2·8	
	7	33·4	7·2	
	8	37·5	1	Doubtful.

TABLE CXCIII.—*Continued.*

H_δ—*Continued.*

Nature of the components.	Number of component.	Distance from centre in A.	Intensity.	Remarks.
s-components . .	8	34·8	1·1	Doubtful.
	7	30·4	1·3	
	6	25·8	2·4	
	5	21·2	2·0	
	4	17·2	1	
	3	11·9	2·1	
	2	7·4	3·2	
	+ 1	+ 2·4	1·3	
	− 1	− 2·4	1·3	
	2	7·4	3·2	
	3	11·9	2·1	
	4	17·2	1	
	5	21·2	2·0	
	6	25·8	2·4	
	7	30·4	1·3	
	8	34·8	1·1	Doubtful.

The symmetry of the resolution picture obtained is clearly shown, but the scale of wave-lengths used does not indicate any means of comparison between the resolutions of the four lines. If the separations are expressed in wave-numbers and not wave-lengths, there appears at once a very interesting and remarkable relationship between them. In Table CXCIV. are given the wave-numbers of the components observed on the long wave side of the undisplaced line, those on the short wave side being omitted since the resolution picture is absolutely symmetrical in each case.

TABLE CXCIV.

H_α.

	ν.	$\Delta\nu$.	Factors.	
p-components .	(15233·2)			
	15218·8	14·4	2 × 7·2	
	15212·8	20·4	3 × 6·8	
	15206·6	26·4	4 × 6·65	
s-components .	15233·2	6·0	1 × 6·0	
	15227·2			

TABLE CXCIV.—*Continued.*

H_β.

	ν.	$\Delta\nu$.	Factors.	
p-components .	20564·8			
	20550·8	14·0	2 × 7·0	
	20536·5	28·3	4 × 7·1	
	20522·5	42·3	6 × 7·05	
	20509·1	55·7	8 × 7·0	
	20495·6	69·2	10 × 6·9	
	20483·0	81·8	12 × 6·8	Doubtful.
s-components .	20564·8			
	20550·4	14·4	2 × 7·2	
	20536·9	27·9	4 × 7·0	
	20523·8	42·0	6 × 7·0	
	20509·1	55·7	8 × 7·0	Doubtful.
	20496·0	68·8	10 × 6·9	
	20483·4	81·4	12 × 6·8	

H_γ.

p-components .	(23032·5)			
	23018·2	14·3	2 × 7·15	
	22997·5	35·0	5 × 7·0	
	22976·4	56·1	8 × 7·0	
	22948·5	84·0	12 × 7·0	
	22927·4	105·1	15 × 7·0	
	22906·4	126·1	18 × 7·0	
	22878·1	154·4	22 × 7·0	Doubtful.
s-components .	23032·5			
	23011·8	20·7	3 × 6·9	
	22981·2	51·3	7 × 7·3	
	22962·2	70·3	10 × 7·0	
	22941·1	91·4	13 × 7·0	
	22912·2	120·3	17 × 7·1	
	22893·8	138·7	20 × 7·0	

H_δ.

p-components .	(24373·1)			
	24343·2	30·9	4 × 7·7	
	24316·1	57·0	8 × 7·1	
	24287·8	85·3	12 × 7·1	
	24257·2	115·9	16 × 7·2	
	24230·1	143·0	20 × 7·15	
	24204·3	168·8	24 × 7·0	
	24176·2	196·9	28 × 7·1	
	24152·3	220·8	32 × 6·9	Doubtful.

TABLE CXCIV.—*Continued.*

Hδ—*Continued.*

	ν.	Δν.	Factors.	
s-components .	(24373·1)			
	24358·8	14·3	2 × 7·15	
	24329·2	43·9	6 × 7·3	
	24302·6	70·4	10 × 7·0	
	24271·3	101·8	14 × 7·3	
	24247·8	125·3	18 × 7·0	
	24220·7	152·4	22 × 6·9	
	24193·7	179·4	26 × 6·9	
	24168·0	205·1	30 × 6·8	Doubtful.

It is quite obvious that the values of $\Delta\nu$ are all integral multiples of a fundamental unit of separation which is very near to 7 cm.$^{-1}$ for the field of 104,000 volts × cm.$^{-1}$ in which the above separations were observed. In view of what was said above as to the proportionality between separation and field strength it follows that it is the fundamental unit of separation which is proportional to the strength of the field. This is a relation of outstanding importance and its significance will be discussed below when the theoretical explanation of the Stark effect is given.

In Fig. 45 are given the resolution pictures obtained with the four hydrogen lines. The components are spaced on a scale of wave-numbers and the length of the lines represents the relative intensities of the components as given in Stark's own tables. It must be remembered that the relative intensities only refer to the components of any one hydrogen line and are not comparable as between two separate hydrogen lines. An interesting fact is to be observed in Fig. 45, namely, that the intensity increases towards the outermost *p*-components, whereas in the case of the *s*-components the intensity increases in the opposite direction.

With reference to the number of components exhibited by the four hydrogen lines Stark draws attention to the great differences of intensity between them, and consequently we must consider the possibility of the existence of other components with less intensity than those recorded. He believes that this is certainly the case with H_α, partly on account of the strong intensity of the nine observed components, and partly by analogy with the other three lines, H_β, H_γ, and H_δ. As far as the last three lines are concerned Stark believes that the number of components is about right, although of course there might exist more components of very weak intensity. In his list one or two of the components were recorded as being doubtful, this meaning that their presence was dubious or, alternatively, that they occupied the position of a possible ghost given by his grating.

Before the results obtained with elements other than hydrogen

come under our notice a brief description may be given of Lo Surdo's method of observation. From an experimental point of view this

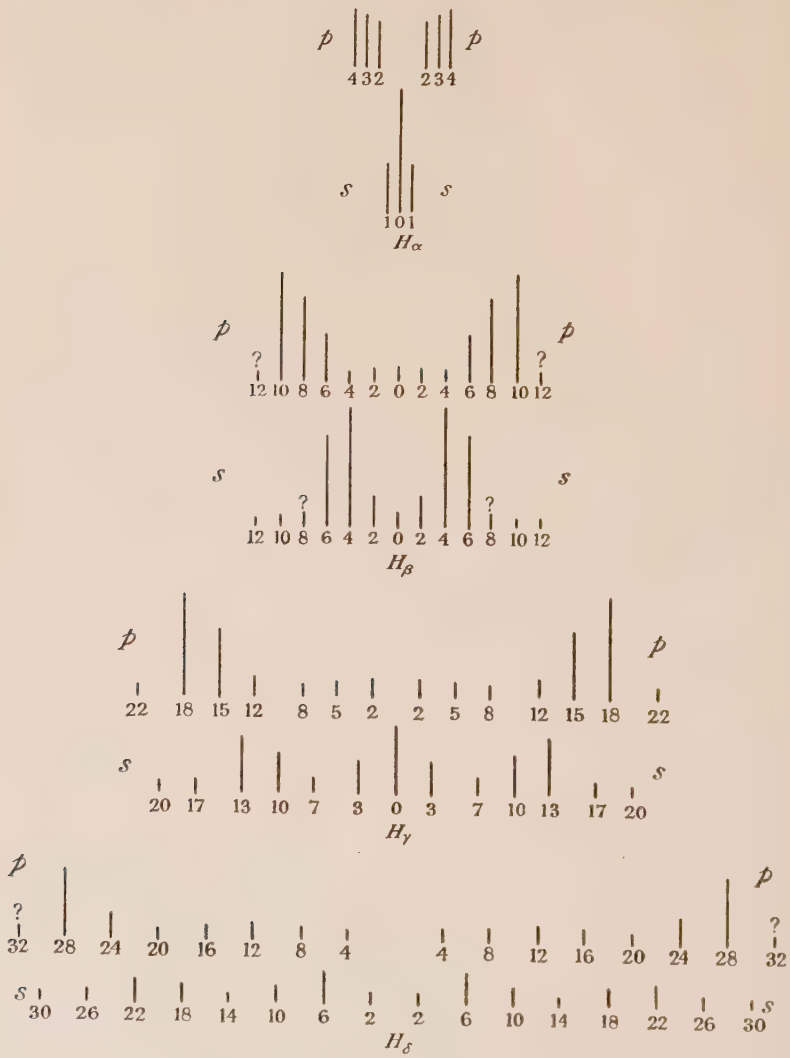


Fig. 45.

method is very much simpler than that of Stark, and the discharge tubes are far easier to construct. Against this must be set the fact that no direct means are available of measuring the field, but this

disadvantage to a great extent is neutralised, since Stark's values for the relation between field strength and separation of the outer components of the hydrogen resolution picture have been published. The strength of the field at any point of the cathode dark space may be determined by measurement of the hydrogen components.

As is well known there is a sharp potential gradient in the first cathode or Crookes' dark space, with the result that any emission of spectral lines in that region takes place in an electric field. Lo Surdo showed that the increase in the potential gradient at a given pressure depends only on the current density of the discharge through the tube. It is necessary that the cathode completely fill the discharge tube in order that the lines of force may be parallel to one another, and Lo Surdo found that under these conditions the length of the cathode dark space is independent of the diameter of the tube.

The construction of the discharge tube is the simplest possible and is diagrammatically shown in Fig. 46. The two electrodes consist of aluminium rods of the same diameter as the internal diameter of the tube and are attached to platinum wires which are sealed into the glass ends of the discharge tube in the usual way. At first Lo Surdo used tubes 4 mm. in diameter but later he reduced this to

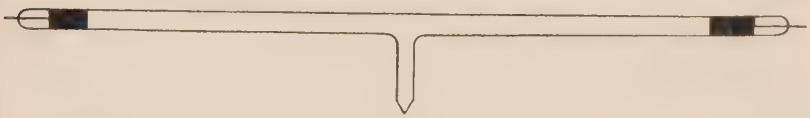


Fig. 46.

1·5 mm. The length of the tubes is about 20 cm. The best results are obtained when the pressure is such that the length of the dark space is about 2 mm.

The discharge must be unidirectional and Lo Surdo used accumulator batteries which gave a potential difference of 5000 to 8000 volts. An induction coil may also be used provided that a rectifying valve is introduced into the circuit.

In using this type of apparatus it will be found that, inasmuch as the electric field is not uniform throughout the cathode dark space, the resolution of the hydrogen lines will be evidenced as a Y-shaped picture, the tail of the Y being of course the unresolved line. This is by no means inconvenient since the strength of the field at any point of the cathode dark space can be determined by the use of Stark's quantitative measurements.

A considerable amount of work on the hydrogen resolution has been carried out by Takamine,[1] who showed that in the case of H_γ the distribution of the components is not absolutely symmetrical with respect to the position of the undisturbed line. More recently

[1] T. Takamine and U. Yoshida, *Mem. Coll. Sci.*, Kyoto, **2**, 137, 321 (1917); T. Takamine and N. Kokubu, *ibid.*, **3**, 271 (1919).

this apparent divergence from the theory as developed below has been explained by Sommerfeld.[1]

Brief reference has already been made to Stark's earlier investigations of the electrical resolution of the spectrum lines of helium, and in general it may be stated that in the case of the spectra of the neutral helium atom the simple laws which were established for hydrogen are not obeyed. There is no need to describe this early work carried out by Stark since more accurate measurements were made at a later date in his laboratory by Liebert. Mention, however, may be made here of his discovery that the diffuse series alone is resolved into components which are very similar to those observed for the diffuse series of lithium, the close analogy being shown in the tables given below. Reference may also be made to the valuable and important work carried out by Takamine and his co-workers,[2] who made use of Lo Surdo's method. The importance of Liebert's work is to be found in the fact that he used the canal ray method and was therefore able to correlate directly together the field strength and the Stark effect with helium. This enabled Stark to measure the resolution of the ionised helium lines by the Lo Surdo method, since this spectrum is not excited by canal rays, using Liebert's measurements of the resolution of the neutral helium lines to determine the strength of the field.

In his work Liebert used discharge tubes which were of the same type as those used by Stark in the measurement of the fine structure of the hydrogen resolution, two tubes being employed, in one of which the distance between the field electrodes was 2·5 mm. and in the other 1·5 mm. The Stark effect is markedly different for the lines of the different series of helium and parhelium as is evidenced by the following data which are quoted from Liebert's paper.

In the case of the principal series of helium (orthohelium) the *p*- and *s*-components exhibit the same displacements and the lines are not resolved but merely displaced. The displacements are given in Table CXCV. for two field strengths.

TABLE CXCV.

HELIUM, PRINCIPAL SERIES.

λ.	*m*.	Shift in A.	
		17,900 volts × cm.$^{-1}$.	27,500 volts × cm.$^{-1}$.
3888·79	2	Too small to measure.	
3187·83	3	,, ,,	,,
2945·22	4	+ 0·20	+ 0·47
2829·17	5	+ 0·57	+ 1·25
2763·90	6	+ 1·27	+ 3·25

[1] *Ann. der Phys.*, **65**, 36 (1921).

[2] T. Takamine and U. Yoshida, *Mem. Coll. Sci.*, Kyoto, **2**, 327 (1917); T. Takamine and N. Kokubu, *ibid.*, **3**, 81 (1918); **3**, 275 (1919); *Proc. Math.-Phys. Soc.*, Tokyo, **9**, 394 (1918).

These values entirely confirm the earlier observations and establish the fact that the lines are not resolved but are displaced towards the red. The displacement, moreover, for a given field strength increases with the order number of the lines and is not proportional to the field strength but increases more rapidly than the field strength.

Exactly the same is true of the lines of the sharp series of helium, the displacement of two of which are given in Table CXCVI.

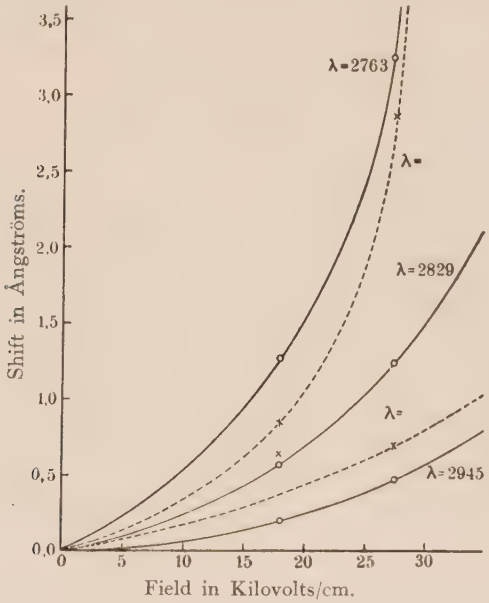


FIG. 47.

(*From "Annalen der Physik," Vol.* 56, p. 593, 1918.)

TABLE CXCVI.

HELIUM. SHARP SERIES.

λ.	*m.*	Shift in A.	
		17,900 volts × cm.$^{-1}$.	27,500 volts × cm.$^{-1}$
3867	5	+ 0·64[1]	+ 0·70
3733	6	+ 0·84	+ 2·57

The divergence of the shift from proportionality with the field strength is well shown in Fig. 47 in which the shift in Ångströms is plotted against kilovolts per cm.

[1] This value is probably too large.

When we come to the diffuse series of helium we find a very different phenomenon. Not only are the lines definitely resolved into *p*- and *s*-components as already found by Stark and Kirschbaum, but the relation between separation and strength of field varies in a remarkable manner.

Liebert measured the resolution in three different field strengths and his results are given in Table CXCVII. In the first case the field was too weak for the separate components to be measured, but he was able in the case of three lines to determine the separation of the outer components with reasonable accuracy.

TABLE CXCVII.

7125 Volts × cm.$^{-1}$.

λ.	*m*.	Distance in A between outer *p*-components.	Distance in A between outer *s*-components.
3819·75	4	3·11	2·28
3705·15	5	3·52	3·22
3634·52	6	3·60	3·54

17,900 Volts × cm.$^{-1}$.

λ.	*m*.	Δλ in A from undisturbed line of *p*-components.	Δλ in A from undisturbed line of *s*-components.
4026·34	3	− 2·98 − 0·21 + 1·93	− 2·73 − 0·35 + 1·98
3819·75	4	− 3·93 1·32 + 1·29 + 3·85	− 3·93 − 1·35 + 1·23 + 3·63
3705·15	5	− 6·60 − 3·51 − 0·68 + 1·18 + 3·63	− 5·69 − 3·19 − 0·76 + 1·75 + 3·95
3634·52	6	− 7·76 − 4·96 − 2·02 + 1·31 + 4·43 + 6·03	− 7·48 − 4·44 − 1·33 + 1·31 + 4·43 + 6·03
3587·57	7	At least 7 components.	At least 7 components.

27,500 Volts × cm.$^{-1}$.

λ.	*m*.	Δλ in A from undisturbed line of *p*-components.	Δλ in A from undisturbed line of *s*-components.
4026·34	3	− 4·34	− 4·24
		− 0·86	− 0·70
		+ 2·91	+ 2·61
3819·75	4	− 8·23	− 5·07
		− 3·08	− 1·52
		+ 0·99	+ 1·53
		+ 5·77	+ 5·28
3705·15	5	− 9·14	− 8·09
		− 5·40	− 4·42
		− 1·09	− 0·01
		+ 3·35	+ 3·60
		+ 7·66	+ 8·19
3634·52	6	− 18·25	− 18·25
		− 14·39	− 14·57
		− 11·85	− 11·92
		− 7·66	− 7·78
		− 5·47	− 5·47
		− 2·28	− 2·28
		+ 0·18	+ 0·18
		+ 2·13	+ 2·13
		+ 5·58	+ 5·58
		+ 9·58	+ 8·72

A glance at Table CXCVII. shows at once an analogy with hydrogen in that the number of components increases in a given field strength with the order number of the lines, but, as can also be seen, the resolution pictures are by no means symmetrical. In Figs. 48 and 49 are shown the relations between the distance between the outer components and the field strength. The relation is a linear one for the two lines $\lambda = 4026$ and 3820, this having been already found for the former by Stark and Kirschbaum, who also noted that the rate of increase in the distance between the components of the line $\lambda = 4472$ is smaller than that in the field strength. For the lines $\lambda = 3705$ and 3634 the rate of increase is greater than that in the field strength.

Liebert also investigated the effect of an electric field on the lines of the principal series of parhelium and he confirmed the observations of Stark and Kirschbaum, who noted that the lines of this series are not resolved, but are shifted towards the shorter wave-lengths, which is the opposite to that observed for the principal series of helium. The amount of this shift increases as the order number of the lines increases, the lines observed being $\lambda = 3964$, 3615, 3448.

In view of the unsymmetrical resolution of the spectrum lines of the neutral helium atom, considerable interest arises with respect to

the resolution of the spectrum lines of ionised helium in view of the close analogy between these and the Balmer series of hydrogen. As was shown in Chapter I. the formula of the 4686 series is

$$1/\lambda = 4N\left(\frac{1}{3^2} - \frac{1}{m^2}\right),$$

which only differs by the factor 4 from the formula for one of the hydrogen series. It is therefore to be expected that the Stark effect for the lines of ionised helium should be very similar to that for the hydrogen lines.

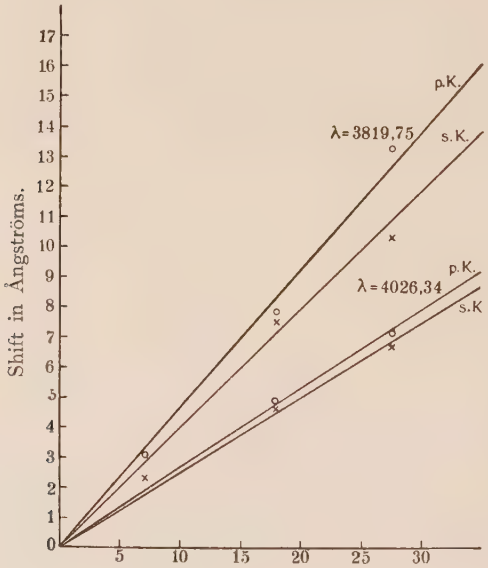


FIG. 48.

(*From "Annalen der Physik," Vol.* 56, p. 597, 1918.)

The first attempt to observe the Stark effect for the ionised helium line $\lambda = 4686$ was made by Evans and Croxson,[1] who used the Lo Surdo method, this being necessary since, as was previously mentioned, the ionised helium lines are not excited by the canal rays. Using field strengths up to 37,000 volts per cm., these authors found that the line was broadened and not resolved into components. The broadening of the line appeared to be symmetrical, the intensity of the outside edges being less than that of the central portion of the line. They found that the width of the line was 3·7 A. when the separation of the components of the H_β line was 7·2 A. Each of the hydrogen

[1] *Phil. Mag.*, **32**, 327 (1916).

components, however, was double and the lines were too diffuse to permit of an accurate measurement of the distance between the outside components. By the use of Stark's values it was calculated that this distance was approximately 10 A., and consequently it seems evident that if the broadening of the 4686 line is entirely due to the electric field, its magnitude is definitely less than one-half that of H_β.

The first to succeed in proving the resolution of this line was H. Nyquist,[1] who made a modification in the design of the Lo Surdo discharge tube. Considerable trouble is experienced in the use of the Lo Surdo apparatus owing to the disintegration of the electrodes

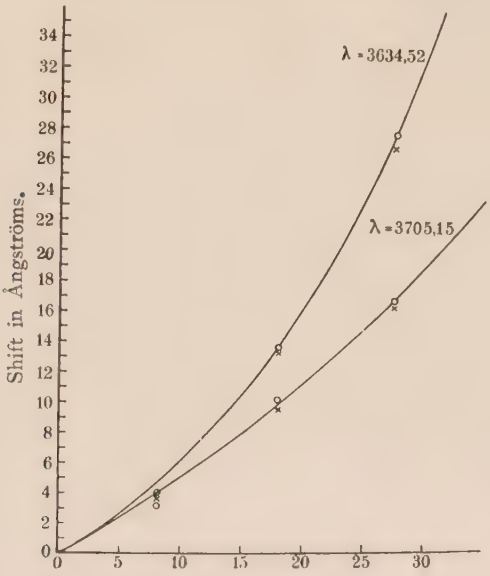


FIG. 49.

(*From "Annalen der Physik," Vol.* 56, p. 597, 1918.)

and the resulting deposition of a metallic film on the glass walls. This is particularly troublesome when the discharge tubes contain one of the rare gases. Nyquist surmounted this difficulty by enclosing the cathode proper in an aluminium tube which fitted into the glass discharge tube. A slot was cut in the aluminium tube to allow the light from the cathode dark space to pass and through a window cemented on to a side tube opposite to the slot. The strength of the electric field was determined by the measurement of the resolution of H_β and H_γ. Nyquist found that the resolution of the 4080 line is analogous to that of H_α in the weak fields. In a field of 100,000

[1] *Proc. Nat. Acad. Sci.*, **3**, 399 (1917); *Phys. Rev.*, **10**, 226 (1917).

volts per cm. two *p*-components were observed with separations of $\pm 3{\cdot}2$ A. relative to the undisturbed line, and one *s*-component in the position of the undisturbed line. The resolution picture, therefore, is completely symmetrical.

This investigation was extended by Stark, Hardtke, and Liebert to the next two lines of the series, namely, $\lambda = 3203$ and 2733. In their first experiments these authors used the modified Lo Surdo tube devised by Nyquist, but later they still further improved the apparatus by the substitution of a silica tube for the aluminium tube. The construction of the cathode is shown in Fig. 50, where A is a copper rod 4 mm. thick with a cap of aluminium, this metal showing the smallest amount of disintegration. The rod A is mounted in a quartz glass tube which extends 15 mm. beyond the aluminium cap on A. A slot 2·5 mm. high and 2·0 mm. wide is cut in this quartz tube in such a position that the lower edge of the slot is 0·5 mm. below the top of the aluminium cap.

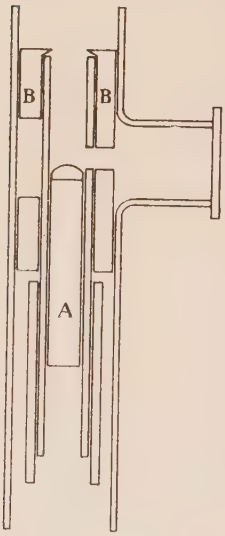


Fig. 50.

The quartz tube is fitted to a brass cylinder B, 3 cm. long with walls 2·5 mm. thick, and this cylinder in its turn fits into the glass walls of the discharge tube. In this cylinder a slot is cut which corresponds exactly to the slot in the walls of the quartz tube. This allows the passage of the light from the first cathode dark space to the spectrograph through a side tube fitted with a quartz or fluorite window. Opposite to the slot a large hole is cut in the brass cylinder. This is very convenient during the adjustment of the apparatus and it also enables observation to be made of the discharge, the length of the dark space, etc.

Below the brass cylinder the quartz tube containing the copper rod is mounted in a glass tube, which is sealed into the walls of the discharge tube, connection with the cathode being made in the usual way by means of a platinum wire electrode. The lower part of the discharge tube is kept cool by immersion in water up to the lower portion of the side tube, water being allowed to drop on the upper side near to the quartz or fluorite window.

A direct current was employed at 4500 volts given by a dynamo (3500 volts) and an accumulator battery (1000 volts), and the best results were obtained with the first cathode dark space extending 3 to 5 mm. and a discharge of 1 to 4 milliamperes. The strength of the field was determined by the resolution of the neutral helium lines measured by Liebert and described above.

It was found that the intensity of the ionised helium lines at $\lambda = 3203$ and 2733 was much smaller than that of the neighbouring

helium lines, and owing to the disintegration of the electrode there was present a marked ultra-violet continuous spectrum. Considerable difficulty was met with in obtaining good photographs, but the values for the two lines given in Table CXCVIII. were obtained from the measurement of the best photographs. Whilst the error may be as great as 25 per cent. it is probably much smaller. The actual strength of the field was 26,600 volts per cm. and in order to compare the separations with those observed by Nyquist for the line $\lambda = 4686$, these have been multiplied by 100000/26600 on the assumption that the separation is linearly proportional to the strength of the field. Nyquist's measurements are included in the table for the purposes of comparison.

TABLE CXCVIII.

λ	26,600 volts × cm.$^{-1}$.		100,000 volts × cm.$^{-1}$.	
	p-components.	*s*-components.	*p*-components.	*s*-components.
4686			+ 3·2 (3) − 3·2 (3)	0 (6)
3203	+ 1·02	+ 0·51	+ 3·8 (5)	+ 1·9 (5)
		− 0·51		− 1·9 (5)
	− 1·02		− 3·8 (5)	
2733	+ 1·35	+ 0·98	+ 5·1 (6)	+ 3·7 (4)
	? + 0·3		? + 1·2 (1)	0 (7)
	? − 0·3			
		− 0·98	? − 1·2 (1)	
	− 1·35		− 5·1 (6)	− 3·7 (4)

The relative intensities are represented by the bracketed figures and the values for the inner *p*-components of $\lambda = 2733$ are uncertain.

It will be noticed at once that the resolution pictures with all three lines are symmetrical, as is the case with the lines of the Balmer series of hydrogen. The very close analogy between the resolutions of the lines of ionised helium and of hydrogen is shown in Fig. 51 which is self-explanatory. It will be seen from this figure that Evans and Croxson were correct in their conclusion that for equal field strengths the separation observed with ionised helium is less than half that observed with hydrogen.

There remains now to be described the Stark effect with other elements, namely, lithium and some of the heavier metals. Reference has already been made to Stark's work on lithium, but before giving his results it is necessary to describe the modifications made in the design of his discharge tube for the purpose of studying the resolution of the spectrum lines of other substances than hydrogen and helium.

The alkali and alkaline earth metals can be examined owing to the fact that their series lines are excited when their salts are exposed to

a rapid stream of canal rays.[1] The luminescence takes place in the space immediately above the surface of the salt. In order to adapt this method to the present purpose, the electrode is prepared in the following way. In Fig. 52 is shown an iron disc mounted on an iron rod. The upper surface of the disc is countersunk as shown and in this depression rests a thin flat disc of platinum pierced with many holes. The whole is then covered with the required anhydrous salt and

FIG. 51.

heated until the salt melts and flows well over and under the platinum. More of the salt is then added and the whole is again melted and allowed to cool. When solidification begins the layer of salt is smoothed and made as flat as possible. A screw thread is cut on the lower end of the iron rod and a small nut is fitted to the screw. The nut is mounted with shellac into the end of a hollow glass plug which is ground into the end of the discharge tube. The exact position of the iron disc is adjusted by means of the screw and, when this has been carried out, the screw and nut are well coated with shellac.

FIG. 52.

If the residual gas in the discharge tube is hydrogen, the salts are reduced to metal with very inconvenient results. It is far preferable to use oxygen, which may of course be obtained by heating potassium chlorate contained in a side tube attached to the discharge tube. Stark employed this apparatus in investigating the effect of the electric field on the lines of sodium, magnesium, calcium, aluminium, thallium, and mercury. Except in the case of lithium the results he obtained were not sufficiently accurate to justify their publication. Two observations, however, must be mentioned. In the first place, the lines of the diffuse series exhibit a greater tendency to be resolved into separate components than the lines of the principal

[1] V. Carlheim-Gyllensköld, *Arch. Math. Ast. och Fys.*, **4**, No. 33 (1908); J. Stark and G. Wendt, *Ann. der Phys.*, **38**, 669 (1912).

and sharp series. In the second place, Stark found that the resolution tends to decrease with increase in atomic weight, but it is remarkable that in a field of 18,000 volts per cm. two members of the diffuse triplets of mercury show definite resolution, in spite of the large atomic weight of this element.

The measurements made by Stark of the resolution of the lines of the diffuse series of lithium are given in detail in Table CXCIX. so as to show the close analogy with that of the helium lines.

TABLE CXCIX.

LITHIUM, 38,000 VOLTS PER CM.

λ.	*m*.	Separation in A. of *p*-components.	Intensity and remarks.	Separation in A. of *s*-components.	Intensity and remarks.
6103·84	2	+ small.	3	+ small.	3
4602·37	3	+ 1·24	8	+ 1·07	8
		− 0·53	1 doubtful.	− 0·53	1 doubtful.
		− 3·43	6	− 3·12	6
4132·93	4	+ 3·56	3	+ 2·98	3
		− 0·71	4	− 0·62	4
		− 4·98	2	− 4·63	2
3915·59	5	+ 6·41	1 uncertain.	+ 6·27	1 uncertain.
		+ 1·82	1 ,,	+ 1·42	1 ,,
		− 2·94	1 ,,	− 2·22	1 ,,
		− 7·21	1 ,,	− 6·45	1 ,,

In measuring the Stark effect for the diffuse series of helium Liebert did not observe the first two lines for which $m = 2$ and 3. These were examined by Stark and Kirschbaum in a field of 28,500 volts per cm. and for convenience in comparing helium and lithium their values for the first four lines are given in Table CC.

A comparison of Tables CXCIX. and CC. shows a remarkable agreement between the Stark effects as exhibited by the two elements. In both cases each line gives the same number of approximately equal *p*- and *s*-components, and this number is equal to $m - 1$, since the doubtful central component of the line $m = 3$ may be ignored. It may further be noted that the distance between the two outer *p*-components is in each line greater than that between the two outer *s*-components. Further, the values of the separations for the two specified fields are very similar for the corresponding lines of both elements. Since the field in the case of lithium is materially larger than that used in the case of helium it follows that the separation for equal field strengths is decidedly smaller in the case of lithium. Indeed this is the only essential difference between the two elements as far as the Stark effect is concerned.

TABLE CC.

HELIUM, 28,500 VOLTS PER CM.

λ.	*m.*	Separation in A. of *p*-components.	Intensity and remarks.	Separation in A. of *s*-components.	Intensity and remarks.
5875·87	2	+ 0·14	4	+ 0·09	4
4471·65	3	+ 1·20	8	+ 1·07	8
		+ 0·04	1 doubtful.	+ small.	1 doubtful.
		− 2·94	6	− 2 63	6
4026·34	4	+ 3·47	5	+ 3·12	5
		− 0·40	5	− 0·40	5
		− 4·23	4	− 4·01	4
3819·75	5	+ 5·34	2	+ 5·16	2
		+ 1·78	3	+ 1·78	3
		− 2·05	3	− 1·69	3
		− 5·96	2	− 5·61	2 broad.

This brings us to the end of the work which has been carried out by Stark's own canal ray method, and there next comes under review some further investigations on the Stark effect on lines of metals which have been carried out by Lo Surdo's method. There are three investigations which may be described, of which the first was carried out by Miss Howell,[1] who used as electrodes rods of various metals 5 mm. in diameter and 1·5 to 2 cm. long. The metallic cathode when bombarded by the rays from the anode gives the spectrum lines of the metal close to the surface, which of course is just the position for the observation of the Stark effect. Equally brilliant spectra are obtained in air, oxygen, and hydrogen, and the last gas was used for the purpose of measuring the strength of the field. The design of the discharge tubes was quite simple and is indicated in Fig. 53, *a*, *b*, and *c*. The side tube and window shown in *b* were used in cases when the metal disintegrated and formed a layer on the walls of the tube. The longitudinal effect was studied by the use of the form shown in *c*.

When the cathode is covered with a thin layer of the anhydrous chloride of the metal, a very brilliant spectrum is obtained, this having already been made use of by Stark and mentioned above. Miss Howell used this method in studying the Stark effect with lithium, calcium, and strontium.

The spectroscope was a three prism instrument with a linear dispersion of 1 mm. = 18 A. at H_γ and 1 mm. = 12 A. at $\lambda = 3950$. The strength of the field was determined from measurements of the resolu-

[1] Janet T. Howell, *Astrophys. Journ.*, **44**, 87 (1916).

tion of H_γ, and it was found convenient to obtain the separation between the outer components by doubling the displacement of the outer component on the short wave side. The discharge from an induction coil was used, together with a rectifying valve, and consequently was not completely unidirectional.

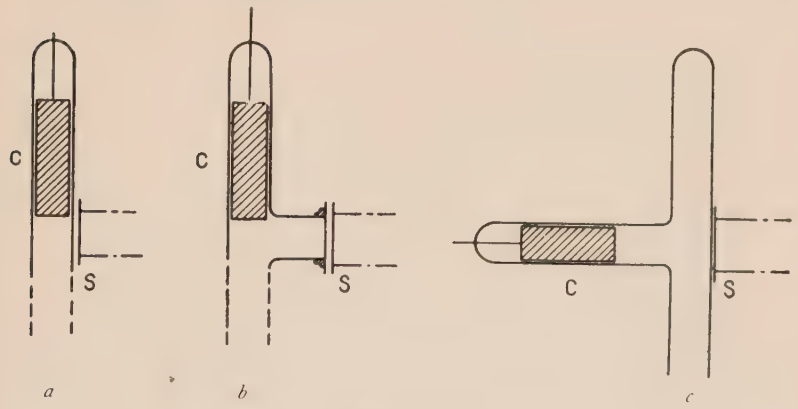


FIG. 53.

In the case of lithium the separations obtained in the transverse effect were in general rather larger than those found by Stark with the same strength of field. The results obtained in the longitudinal effect with a field of 20,000 volts per cm. are given in Table CCI.

TABLE CCI.

λ.	Separation in A. *p*-components.	Intensity.	Separation in A. *s*-components.	Intensity.
4602·37	+ 0·57	8	+ 0·34	6
	− 2·01	6	− 1·53	3
	+ 1·16	1	+ 0·77	1
4132·93	− 0·26	5	− 0·26	5 unpolarised.
	− 1·99	0	− 1·50	0

The polarisation of the components is a new phenomenon, since, as has already been stated, the components observed in the longitudinal effect are unpolarised with both hydrogen and helium.

Miss Howell found no evidence of any electric effect with the lines of the diffuse series of calcium at $\lambda = 4457$, 4435, and 4425. On the other hand, the H and K lines ($\lambda = 3968{\cdot}63$ and 3933·83), which belong to the principal series gave in a field of 20,000 volts per cm. the separations shown in Table CCII.

TABLE CCII.

TRANSVERSE EFFECT.

λ.	*p*-components.	Intensity.	*s*-components.	Intensity.
3968·3	+ 0·22	6	+ 0·16	6 unpolarised.
	− 0·86	2	− 0·74	2
3933·83	+ 0·22	9	+ 0·22	9 unpolarised.
	− 0·92	3	− 0·74	3

LONGITUDINAL EFFECT.

3968·63	+ 1·27	3	+ 1·23	3 unpolarised.
	+ 0·01	8	− 0·02	8 ,,
	− 1·17	0	− 1·11	0 ,,
3933·83	+ 1·42	4	+ 1·38	4 ,,
	+ 0·06	9	− 0·02	9 ,,
	− 1·30	1	− 1·26	1 ,,

This result does not conform to Stark's generalisation that the diffuse series show greater resolution than either the sharp or principal series, and, further, the separation is very large for an element of so high an atomic weight (Ca = 40). It may be noted that Stark found no resolution of the H and K lines in the transverse effect,[1] and this raises the question as to whether the electric effect is the same under the different conditions of the two experimental methods, namely, those of Stark and of Lo Surdo. This question has not yet found a satisfactory answer.

It may be mentioned that Miss Howell was not able to detect any electric effect in the cases of magnesium, strontium, zinc, aluminium, iron, and nickel. She quite rightly pointed out that the absence of any effect with these metals indicated the need for further work with more intense light sources and greater dispersion.

The realisation of these improved conditions was achieved by Anderson [2] with metals of relatively high melting-points. An added importance attaches itself to the study of the Stark effect with such metals as iron, nickel, chromium, vanadium, and titanium, since their spectra are of special significance in solar spectroscopy. If some of their lines exhibit a Stark effect it would at once be possible to determine whether electric fields exist in the solar atmosphere.

The discharge apparatus used by Anderson is illustrated in Fig. 54 and consists of a bell-jar about 15 cm. in diameter and about 30 cm. high, which is luted on to a strong glass plate with two holes

[1] *Ann. der Phys.*, **43**, 1017 (1914).
[2] J. A. Anderson, *Astrophys. Journ.*, **46**, 104 (1917).

drilled in it. In one of these holes is sealed a glass tube which connects with a high vacuum oil pump, whilst in the other is sealed a wider glass tube having a platinum electrode sealed in at the lower and closed end. This tube is 2·5 cm. in diameter and tapers to 1·5 cm., in order to form a seat for the ground joint with the silica tube D. At its upper end D is connected by a ground joint to the short and wider silica tube C. The cathode consists of two parts, B, made of iron, and *b*, of the metal to be studied, and rests on the top of the tube D. The short silica tube C has a vertical slot cut in it, about 1 mm. in width, which extends down to the level of the top surface of the cathode proper, *b*, this being necessary to allow the passage of the light from the first cathode dark space. The tube C must be ground truly cylindrical inside and must have a diameter which is about 0·1 mm. larger than that of the cathode *b*, these conditions being most important. Connection between the iron cathode B and the lower platinum electrode is effected by means of a fine platinum wire.

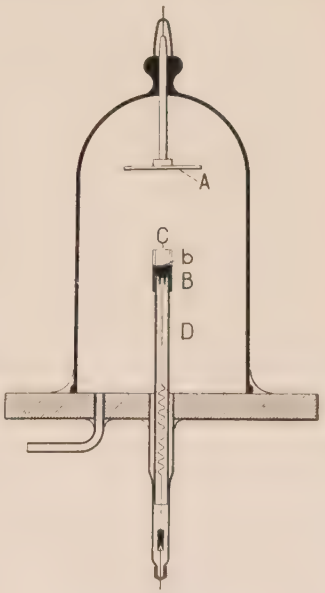


FIG. 54.

The anode A consists of a massive aluminium disc mounted on a rod of the same metal, which is connected to a platinum wire sealed in at the end of a short glass tube. This tube is ground in to a hole drilled through the knob at the top of the bell-jar, the joint being luted with water-glass.

In his investigations Anderson used a direct current from eight generators at about 6400 volts, with a resistance of about 32,000 ohms in series, and adjusted the pressure so that the cathode dark space extended over about 4 mm. With one of the above-mentioned metals as cathode the initial current is about 100 milliamperes, and with manganese it is a little larger, whilst with magnesium it is almost 200 milliamperes. During the first minute the current decreases rapidly and in about two minutes it becomes steady at about 40 milliamperes, the temperature of the cathode proper rising in the meantime to 800°-1000°. The whole of the cathode dark space and most of the negative glow are confined within the tube C.

Considerable heating of the apparatus takes place and in order to protect the bell-jar from unequal heating a sheet brass cylinder, 9 cm. in diameter and 18 cm. high, is placed round the cathode and rests on the glass plate. This cylinder reaches to within about 2·5 cm. from the anode and has a hole cut in it opposite the slot in

the silica tube C. The heating of the bell-jar is then much slower and more uniform, with the result that the discharge can be passed continuously for thirty to sixty minutes without danger. It is advisable to keep the glass-silica ground joint below the glass plate cool by immersion in water, in order to guard against damage arising from the unequal coefficients of expansion of glass and silica.

A very important factor is the correct relationship between the sizes of the tube C and the cathode *b*. If *b* is too small the discharge tends to pass from the iron cathode B in between *b* and C. If, on the other hand, *b* and C are in contact, then, when C is red-hot, C begins to act as cathode and no result can be obtained. Great care must be taken in adjusting the relative sizes of the two so that there is no contact between C and *b*, even when the latter is white-hot. As already stated there must be an annular space of 0·1 mm. between the two when cold.

When the apparatus has been in use for several observations the tube C becomes coated with a metallic film with the result that a short circuit is unavoidable. The only remedy is to dismantle and clean the apparatus. After a short time the cathode *b* becomes hollowed out into a flat-bottomed dish with a rim 0·5 to 1 mm. thick. Since this interferes with the passage of the light this rim must occasionally be removed.

The apparatus was used with an atmosphere of oxygen, since it was found that brighter spectra were obtained with this gas. Hydrogen lines were, however, always visible, and the resolution of these was used to determine the strength of the field. As was pointed out by Takamine and Yoshida,[1] the strength of the field in an ordinary narrow Lo Surdo tube varies approximately as the square of the distance from the negative glow, with the result that the hydrogen components appear as parabolic curves with their vertices in the negative glow. With the above apparatus, on the other hand, the field strength varies almost linearly with the distance from the negative glow, with the result that the components of the hydrogen lines appear on the resolution picture as straight lines. This is extremely convenient, since with other elements it is possible at once to determine whether the displacement varies linearly with the field strength or not by observing whether the components are straight lines or curves.

In his paper Anderson only gives the results of his observations with chromium, and in this work he used a plane grating (4-inch with 14,438 lines to the inch) so mounted that the third order was obtained of from $\lambda = 5000$ to $\lambda = 3000$, and the dispersion varied from 1 mm. = 5·2 A. to 1 mm. = 3·0 A. With short exposures lines

[1] *Mem. Coll. Sci.*, Kyoto, **2**, 137, 335 (1917). The actual relation can be expressed as follows: If E_0 be the field strength at the end of the dark space, E the field strength at any point in the dark space, d the distance of that point from the cathode, and d_0 the length of the dark space, then $E - E_0 = k(d_0 - d)^2$, where k is a constant.

having a separation of 0·1 A. could be resolved, whilst with longer exposures the resolving power was reduced by the effect of temperature variations to from 0·15 to 0·20 A.

An interesting phenomenon was observed in the investigation with chromium and subsequently the same was also found with iron and nickel. At first very little Stark effect was noticed. The normal arc lines were always present, but of the electrically sensitive lines only faint traces of the groups at $\lambda = 4129$, 4111, and 4098 could be seen. By chance a photograph was obtained which showed these groups with an intensity about 100 times as great as the other lines, without any marked increase of intensity of the normal arc lines. After many failures to reproduce this result it was finally found that after about six consecutive runs a sensitive condition was developed, which persisted in subsequent exposures until it became necessary to clean the apparatus, owing to the deposition of the metallic film on the tube C. This phenomenon is undoubtedly connected in some way with the disintegration of the cathode, since the deposition of the metallic film on the tube C and the hollowing out of the cathode become much more rapid when this sensitive condition is established. The appearance of the cathode dark space is also altered, becoming much more luminous.

Anderson did not succeed in explaining this phenomenon, but the following suggestion may tentatively be put forward. It has been found that when the electric discharge is passed through vacuum tubes in the presence of a film of nitride on the electrodes, the nitride is decomposed and some of the nitrogen atoms are disintegrated with the formation of small quantities of helium, some neon also being formed.[1] It is well known that the disintegration of the electrodes is far more pronounced with the rare gases than it is with diatomic gases. In view of the undoubted connection between Anderson's sensitive state and the cathodic disintegration it may be suggested that during the quiescent period before the sensitive state is established the atomic disintegration of nitrogen is slowly taking place. When the amount of rare gases present is sufficient, the marked increase in cathodic disintegration suddenly sets in, a condition which obviously will favour the increased intensity in the luminosity of the cathode dark space. This suggestion finds some support in an observation by Takamine[2] that the more intense spectra are obtained in a similar apparatus presently to be described when the residual gas is air. He attributes this to the presence of nitrogen.

Anderson describes in his paper the Stark effect for 74 lines given by a chromium cathode in the sensitive state between $\lambda = 5330$ and $\lambda = 3719$. The exposures varied from a few minutes in the ultra-violet region to about 40 minutes in the region $\lambda = 4800$-5330.

[1] E. C. C. Baly and R. W. Riding, *Proc. Roy. Soc.*, **109**, A, 180 (1925); see also *Nature*, **118**, 625 (1926).

[2] *Astrophys. Journ.*, **50**, 1 (1919).

TABLE CCIII.

Chromium.

λ.	Int.	*p*-Components.			*s*-Components.		
		Δλ.	Int.	Rate of displacement.	Δλ.	Int.	Rate of displacement.
5330·18	1				+ 0·38	1	=
5329·94	1	− 0·16	2	?			
5329·34	1	+ 0·11	4	+	− 0·32	4	+
5328·52	4	+ 0·16	10	+	+ 0·14	5	+
					0·00	5	
5324·19	1	+ 0·43	3	?			
5298·92	1	+ 0·49	8	+			
5298·43	2	− 0·06	3	?	− 0·03	5	?
5298·18	2	− 0·28	1	?	− 0·12	8	−
5297·50	3	− 0·34	10	=	+ 0·17	2	?
					− 0·27	1	?
5296·88	1	− 0·04	2	?	− 0·03	4	?
5280·81	1	+					
5276·16	2	0·00	3		+ 0·45	3	=
					− 0·03	6	?
5275·92	2	− 0·24	6	+	− 0·18	3	+
5275·44	1	− 0·12	2	=	− 0·20	2	=
5056·93	1	+ 0·42		=			
5055·69	2	+ 0·77	2	=	+ 0·54	2	=
		− 2·19	1	=	+ 0·03	2	=
5028·37	1	+ 0·92	3	=			
5027·74	2	+ 0·41	2	=			
		+ 0·06	2	=	+ 0·21	4	=
		− 1·60	3	=			
5005·81	2	+ 1·50	3	=			
		+ 0·53	1	=	+ 0·31	3	=
		− 1·41	4	=	− 0·43	3	=
4984·97	1	+ 0·30		=	Complex.		
4983·84	1	+ 0·54		=	,,		
4948·25	2	+ 0·34		=	,,		
4900·81	1	+ 0·30		=			
4649·59	3	+ 0·18		−			
4494·92	2	+ 0·54		=	− 0·25		=
4490·86	1	− 0·32		=			
4472·03	2	+ 0·65		=	Complex.		
4453·96	2*h*	+ 0·79		=	− 0·43		=
4423·44	1	Complex.			Complex.		
4423·15	2	,,			,,		
4422·68	3	,,			,,		
4389·37	2	− 0·11		?	− 0·11		?
4353·97	3	+ 0·86		=	+ 0·86		=
4309·05	2	+ 0·71		+	+ 0·71		+
4216·45	3	− 0·15		=	Complex.		
4216·14	3	− 0·13		=	,,		
4215·20	3	− 0·20		=	,,		
4214·89	3	− 0·13		=	,,		
4136·25	1	+ 0·08		?	+ 0·08		?
4130·79	1	+ 0·40		?	+ 0·40		?
4130·13	3	+ 0·26	6	=	+ 0·26	2	−

TABLE CCIII—*Continued.*

λ.	Int.	*p*-Components.			*s*-Components.		
		Δλ.	Int.	Rate of displacement.	Δλ.	Int.	Rate of displacement.
4129·36	7	+ 0·39	8	+	+ 0·46	3	=
					+ 0·33	4	=
					+ 0·20	4	=
					+ 0·06	4	=
					− 0·06	5	=
4128·34	1	− 0·47	6	+	− 0·51	2	+
4117·08	2	+ 0·13		?	+ 0·13		?
4112·18	1				+ 0·58	2	=
4111·82	3				+ 0·11	2	+
					− 0·21	2	=
4111·49	4	+ 0·59	10	=	− 0·69	2	+
4111·02	5				+ 0·23	10	=
4110·75	1	− 0·78	10	=			
4103·40	1	+ 0·06	1	?	+ 0·06	1	?
4098·31	4	+ 0·84	8	=	+ 0·84	2	−
4098·11	4				+ 0·19	7	+
4097·80	3	− 0·68	8	+	− 0·18	7	−
4097·41	1						
4096·94	1				+ 0·21	2	=
4013·99	3	− 0·54		=	− 0·66	1	=
4013·26	4	− 0·56		=	Complex.		
4011·96	4	− 0·55		=	− 0·44		
3929·87	1	+ 0·06		?	0·00		
3926·20	1	− 0·16		=	Complex.		
3896·14	1	− 1·54		+	+ 0·06		?
3870·28	4	+ 0·11		?	− 0·16		=
3865·02	4	+ 0·25		=			
3863·11	1	+ 0·29		?	+ 0·04		?
3862·07	2	− 0·42		−	+ 0·18		=
3750·14	1	+ 0·63		=	+ 0·29		?
3747·41	5	+ 0·32		=	− 0·42		−
3744·73	1	− 0·29		=			
3725·13	2	+ 0·91		=	− 0·13		=
3731·85	5	+ 0·40		−			
3730·09	2	− 0·96		=	Complex.		
3722·83	2	+ 1·07		+			
3720·74	5	+ 0·48		=	Complex.		
3719·12	2	− 0·76		=			

and probably more lines would have been observed with longer exposures. Most of the lines observed are not to be found in the published tables of wave-lengths of chromium lines, and the question arises as to whether these lines are really due to chromium. He gives valid reasons for believing that they are actually due to chromium. The wave-lengths of these lines and the magnitude and nature of the Stark effect are given in Table CCIII.

In Table CCIII. the first column contains the wave-lengths of the undisplaced lines, with their relative intensities in the second column. The third column contains the displacements of the *p*-components reduced to a field strength of 12,000 volts per cm., in the fourth column are given the intensities of the components in the stronger part of the field, whilst the fifth column indicates how the displacement varies with the strength of the field. The sign + indicates that the displacement is proportional to a higher power of the field strength than the first, the sign = indicates that the displacement is roughly proportional to the first power, whilst the sign − indicates that the displacement varies more slowly than the first power of the field strength. In a few cases where the displacement was very small, or the displaced component happened to overlap a neighbouring nitrogen band line, a question mark appears in the fifth column. The last three columns contain the similar data for the *s*-components.

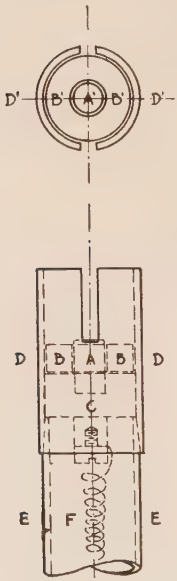


Fig. 55.

There are several lines which only give one type of component. For example, the lines at $\lambda = 4110{\cdot}75$ and 4097·80 have only *p*-components, whilst the lines at $\lambda = 4112{\cdot}18$, 4111·82, 4111·02, 4098·11, 4097·41, and 4096·94 have only *s*-components. The two lines at $\lambda = 4111{\cdot}02$ and 4098·11 are peculiarly interesting, for the *p*-component of $\lambda = 4098{\cdot}11$ can be traced for only a very small fraction of the distance through the dark space, whilst the line $\lambda = 4111{\cdot}02$ can be traced faintly nearly all the way across to the cathode, although the intensity progressively diminishes. In a very weak field, therefore, both these lines are almost completely unpolarised; as the field strength increases, they gradually become polarised, the line $\lambda = 4098{\cdot}11$ reaching complete polarisation in a much weaker field than the line $\lambda = 4111{\cdot}02$.

In another paper Anderson records the Stark effect for some of the lines of nickel,[1] but as this metal has been more extensively studied by Takamine this brief reference is sufficient. Takamine,[2] who investigated many metals, used an apparatus similar to that designed by Anderson, but the diameter of the cathode was reduced from 13 mm. to from 2 to 5 mm. The detailed construction of the cathode is shown in Fig. 55, where A is a cylinder of the metal to be studied, which is fixed in the iron frame C. Resting on top of the iron frame C is a disc of fused silica B with a central hole through which the cathode proper A passes and projects about 0·3 mm. above the upper surface of B. D and E are silica tubes ground to fit tightly together and in D is cut a vertical slot, about 1 mm. in width, which extends down to

[1] *Phys. Rev.*, **9**, 575 (1917). [2] *Astrophys. Journ.*, **50**, 23 (1919).

the level of the upper surface of B. The upper end of this slot is covered by a small piece of metal. F is the platinum wire making connection with the electrode below. In all other respects the apparatus is essentially the same as that used by Anderson. The pressure was reduced until the Crookes dark space had a length of 1 to 2 mm. Direct current was supplied by a set of high potential generators, each giving 800 volts, connected in series. The number of dynamos used varied from 16 to 24. By the use of suitable water resistances the current in general was maintained between 40 and 20 milliamperes. In order to avoid excessive heating, the discharge was passed intermittently and the bell-jar was cooled by means of an electric fan.

The intensity of the field was determined from measurements of the separation of the outermost components of H_β, H_γ, and H_δ, and the maximum value at the cathode (F_{max}) varied from 75,000 to 28,000 volts per cm. With the smaller cathode the distribution of the field strength was not linear, as was found by Anderson, but parabolic.

As mentioned above, it was found that the spectra of the metallic cathodes were obtained with greatest intensity when the residual gas was air, and this increased effect was attributed to the presence of nitrogen.

Takamine studied the Stark effect with copper, silver, gold, magnesium, molybdenum, tungsten, manganese, iron, nickel, and cobalt, and no affected lines were observed in the spectra of manganese and tungsten. One of the most interesting cases is that of silver, which is remarkably similar to that of helium in the behaviour of its lines in the electric field. The resolutions are given in Table CCIV., the values of the maximum strength of field being set out for each line in the last column.

As in the case of helium the lines of the diffuse series ($\lambda = 4213$, 4211, 4055, 3811, and 3682) show resolution into components, whilst the lines of the sharp series ($\lambda = 4669$, 4476, 3982, and 3841) only show displacement in one direction. There are one or two anomalies, such for example as the behaviour of the *p*- and *s*-components on the short wave side of the lines $\lambda = 3811$ and 3682. In a weak field these are displaced approximately in proportion to the field strength; as the field increases this law ceases to hold, and in strong fields the displacement becomes practically constant. A further interesting fact is to be noticed in the relative intensities of the *p*- and *s*-components of these lines. As can be seen, these are reversed, that is to say, the ratio of intensities of the two first longer wave *p*-components is the reciprocal of the ratio of the intensities of the two longer wave *s*-components.

As was pointed out by Koch [1] and later by Stark,[2] new lines are to be found in the spectrum of helium when emission takes place in a

[1] *Ann. der Phys.*, **48**, 98 (1915). [2] *Ibid.*, **56**, 577 (1918).

TABLE CCIV.

SILVER.

λ.	*p*-Components.		*s*-Components.		Fmax.
	λ.	Int.	λ.	Int.	
4668·58	+ 0·03	10	+ 0·03	10	48,000
4476·31	+ 0·04	10	+ 0·02	10	48,000
4226·55	+ 2·33	3	+ 2·14	3	56,000
4212·76	+ 2·53	3	+ 2·70	3	56,000
	0	5	0	5	
	− 3·47	3	− 2·98	3	
4210·87	+ 4·23	5	+ 3·99	5	56,000
	0	6	0	6	
	− 3·80	10	− 1·91	10	
			− 3·54	3	
4206·88	+ 1·46	2	+ 1·28	2	55,000
4081·7	+ 0·88	3	+ 0·86	3	55,000
4055·44	+ 3·33	10	+ 3·29	10	56,000
	0	4	0	3	
	− 5·20	8	− 3·21	6	
			− 4·49	2	
3981·87	+ 0·13	3	+ 0·14	3	48,000
3840·74	+ 0·15	2	+ 0·08	2	48,000
3810·85	+ 11·04	3			48,000
	+ 5·21	3	+ 5·36	4	
	0	5	0	5	
	− 0·41	2	− 0·43	10	
	− 1·77	10	− 1·40	3	
	− 7·15	6	− 4·78	3	
3682·45	+ 13·00	1			48,000
	+ 4·35	2	+ 4·90	1	
	0	4	0	2	
	− 0·69	1	− 0·84	5	
	− 1·59	6	− 1·84	1	
	− 5·00	2			

strong field, owing to the fact that the principle of selection no longer is valid (see p. 110). The same is found in the case of silver, and the lines at $\lambda = 4207$ and 4082 belong to this type, since they are not visible in the arc spectrum of this element.

The results obtained with copper were somewhat analogous to those obtained with silver, the two lines at $\lambda = 3688{\cdot}60$ and 3654·59 of the diffuse series ($m = 6$) being resolved into components. The lines ($m = 5$) of the same series at $\lambda = 4063{\cdot}50$, 4062·14, and 4022·83 are shifted towards the red, whilst the lines ($m = 4$) at $\lambda = 5220{\cdot}25$, 5218·45, and 5153·33 are shifted towards the violet.

Only three lines of gold were found to exhibit the Stark effect, and in the case of magnesium four lines at $\lambda = 4703{\cdot}3$, 4352·2, 3097·1, and 3093·1 are displaced towards the red,[1] whilst the shift in the opposite direction takes place with the line at $\lambda = 4571{\cdot}3$ and the

[1] Takamine and Kokubu, *Mem. Coll. Sci.*, Kyoto, **3**, 173 (1918).

group at $\lambda = 3868{\cdot}4$, $3832{\cdot}5$, and $3829{\cdot}5$, which is the fourth member of the diffuse series of triplets.

Molybdenum shows many lines which exhibit the Stark effect, and these are given in Table CCV. :—

TABLE CCV.

MOLYBDENUM.

λ.	*p*-Components.		*s*-Components.		F in volts per cm.
	λ.	Int.	λ.	Int.	
5544·78	+ 0·34	1	+ 0·49	1	38,600
5406·64	+ 0·49	1	+ 0·35	1	,,
5367·30	− 0·48	1	+ 0·57	1	,,
	0	1	0	1	
	− 1·22	2	− 0·60	1	
			+ 0·48	1	
5264·50	+ 0·43	4	+ 0·43	1	,,
	− 1·22	2	− 1·40	5	
5260·76	+ 0·81	10	+ 0·64	10	,,
5245·71	− 0·10	4			,,
5243·01	+ 1·07	3	+ 0·32	3	,,
	0	2			
5241·09			+ 0·47	1	,,
			0	1	
			− 0·50	2	
5238·41	− 1·48	10	+ 0·34	4	,,
			− 1·41	3	
5174·35	− 0·33	6	− 0·33	6	,,
5173·14	− 0·13	5	− 0·04	5	,,
5171·33	+ 0·49	4	+ 0·94	2	,,
4764·64	+ 0·25	3	+ 0·25	3	,,
4758·71	− 0·13	2			,,
4688·41	− 0·20	3	− 0·20	3	,,
4652·49	+ 0·42	4	+ 0·33	3	,,
4582·69	0	2	− 0·49	2	,,
	− 0·89	3			
4567·87	+ 0·20	1	+ 0·22	1	,,
4535·09	+ 0·53	3	+ 0·58	3	,,
4529·53	+ 2·09	1	+ 1·53	2	,,
	+ 0·41	2	0	2	
			− 0·34	1	
4290·40	+ 0·47	3	+ 0·36	3	,,
4284·79	+ 1·45	4	− 1·80	2	,,
	0	2	+ 0·18	3	
	− 0·13	2	− 1·76	3	
	− 1·78	3			
4157·58	+ 0·92	4	+ 0·81	2	,,
	0	2	0	2	
	− 0·47	3			
4071·54	− 1·17	1	− 1·09	1	,,
4060·4	− 1·01	3	− 0·62	3	,,
4032·65	− 1·51	3	− 1·07	3	,,
4028·85	− 1·49	4	− 1·06	4	,,
4025·64	+ 0·41	1	+ 0·39	1	,,
4017·50	− 0·44	2	− 0·18	2	,,

Two points may be mentioned with respect to Table CCV. In the first place, the same complementary phenomenon of intensity as was noted in the case of the silver lines at $\lambda = 3811$ and 3682 is shown by the molybdenum lines at $\lambda = 5264{\cdot}50$ and $5238{\cdot}41$. Further, the p-component of the line at $\lambda = 5238{\cdot}41$ behaves like the s-component of the line at $\lambda = 5364{\cdot}50$ and vice versa.[1]

Takamine also observed the Stark effect with fifty lines of nickel between the wave-lengths $\lambda = 5588$ and $\lambda = 3826$, and forty-eight lines of cobalt between $\lambda = 5638$ and $\lambda = 3665$. Some lines of sodium, nitrogen and oxygen were also noted as being shifted in the electric field.

In the case of iron eleven lines between $\lambda = 5455$ and $\lambda = 5133$ showed the Stark effect, but this was very small compared with the effects noted with the other elements already dealt with. A very interesting fact was discovered in the unmistakable connection between the Stark effect and the pole effect. In Table CCVI. are given the two effects for the eleven lines observed by Takamine, the values for the pole effect being those of St. John and Babcock.[2]

TABLE CCVI.

λ.	Pole effect.	Stark effect for 29,800 volts per cm.	
		p-Component.	s-Component.
5455·435	− 0·016	− 0·35	− 0·38
5445·040	− 0·020	− 0·06	− 0·06
5424·057	− 0·027	− 0·13	− 0·12
5415·189	− 0·030	− 0·11	− 0·06
5410·900	− 0·026	− 0·02	− 0·04
5404·131	− 0·025	− 0·05	− 0·05
5367·455	− 0·025	− 0·13	− 0·05
5364·859	− 0·028	− 0·06	—
5324·196	+ 0·015	+ 0·05	+ 0·05
5162·312	+ 0·030	+ 0·73	+ 0·28
5133·675	− 0·045	− 0·14	− 0·15

As is obvious from the values given in Table CCVI., there is complete agreement as to the direction of displacement in both the Stark and pole effects. There is also a fairly good quantitative agreement between the two, except in the case of the three lines at $\lambda = 5455$, 5424, and 5162. As far as the first line is concerned this is due to the fact that there are two lines at $\lambda = 5455{\cdot}614$ and $5455{\cdot}435$, the latter being an "e" line and shifted to the violet in the pole effect. Since this close pair was not resolved in Takamine's plates, his measurement

[1] This phenomenon has been explained on Bohr's correspondence principle by A. Rubinowicz, *Zeitsch. für Phys.*, **5**, 331 (1921).

[2] *Astrophys. Journ.*, **42**, 231 (1915); **46**, 138 (1917).

of the Stark effect for the unresolved line is subject to considerable error. Takamine also gives a comparative table of the two effects for eight nickel lines and these indicate a similar qualitative agreement between the two.

Attempts were made to determine whether any correlation exists between the Stark effect and the pressure shift effect, without, however, any conclusive result. A comparison of Duffield's observations of the pressure effect on the lines of copper, silver, gold, iron, and nickel with the present observations would seem to indicate that in many cases the Stark effect is involved as one of the contributory causes of the pressure effect. Duffield classifies the lines into two groups, one of which is strengthened as the pressure increases and the other is weakened. All the lines which exhibit the Stark effect belong to the second group. On the other hand, many lines are broadened unsymmetrically at high pressures and are not affected by an electric field. The relation between the two effects, therefore, is not so simple as between the pole and Stark effects.

Takamine discusses the Stark effect in relation to different spectral series, although of the metals he investigated copper and silver are the only two for which the series have been identified. In general, his results confirm Stark's observations that the diffuse series show complex resolution whilst the sharp series are displaced in one direction, a phenomenon which is very pronounced in the case of helium. The direction of displacement is of considerable interest. The lines of the sharp series of silver are all shifted towards the red, whilst in the case of copper the lines of both the sharp and diffuse series change direction of displacement in passing from $m = 4$ to $m = 5$. This is also the case with magnesium, since the group $\lambda = 3838{\cdot}4$, $3832{\cdot}5$, and 3829, which is the fourth member of the diffuse series, is displaced to the violet, whilst the fifth member containing the lines $\lambda = 3097{\cdot}1$ and $3093{\cdot}1$ is shifted towards the red.

Finally, it may be noted that the similarity of the Stark effect of members of the same chemical family is very striking when the following groups are compared: copper, silver, and gold; chromium and molybdenum; iron, nickel, and cobalt.

In concluding this account of the experimental investigation of the Stark effect, reference may be made to certain other papers which have not been previously mentioned.[1]

The Theory of the Stark Effect.—We may now discuss the theoretical explanation of this phenomenon, and it will be convenient to

[1] "Hydrogen," U. Yoshida, *Mem. Coll. Sci.*, Kyoto, **4**, 187 (1920). "Secondary Spectrum of Hydrogen," M. Kiuti, *Japanese Journ. Phys.*, **1**, 29 (1922). "Hydrogen and Helium," J. S. Foster, *Phys. Rev.*, **20**, 214 (1922); **23**, 667 (1924). "Helium," W. Tschulanowsky, *Zeitsch. für Physik*, **16**, 300 (1923). "The D Absorption Lines of Sodium," R. Ladenburg, *Zeitsch. für Phys.*, **28**, 51 (1924). "Oxygen and Argon," E. Botteher and F. Tuczek, *Ann. der Phys.*, **61**, 107 (1920). "Argon, Iodine, and Nitrogen," W. Steubing, *Phys. Zeitsch.*, **23**, 427 (1922). "Broadening of Spectrum Lines, and Stark Effect," M. Kimura and G. Nakamura, *Japanese Journ. Phys.*, **2**, 61 (1923). "Apparatus and Methods of Observation," F. Tuczek and W. Heuck, *Ann. der Phys.*, **63**, 766 (1920); E. Gehrcke, *Zeitsch. tech. Phys.*, **3**, 93 (1922).

re-state the conclusions which have been arrived at from the experimental results described above.

1. Every hydrogen line of the Balmer series is split into a definite number of components.

2. The number of components increases with the series number of the line.

3. The components are linearly polarised when viewed transversely, some being polarised parallel to the field and some perpendicularly to it, this definition of polarisation referring to the direction of the electric vibration in the light ray.

4. When viewed longitudinally, only the *s*-components are visible, and these are unpolarised.

5. In general, the intense *p*-components lie on the outside and the intense *s*-components towards the inside of the resolved group.

6. In the case of hydrogen the distribution of the components, both as regards number and polarisation, is symmetrical with reference to the parent line, but this symmetry tends to vanish in the case of other atoms.

7. In the case of hydrogen the distances in wave-numbers of the components from the central undisturbed line are integral multiples of a definite smallest distance, and this interval is the same for all hydrogen lines.

8. The resolution and the smallest line interval increase proportionately with the external field.

The theoretical explanation of this phenomenon for atoms of the hydrogen type was obtained independently by Schwarzschild [1] and by Epstein,[2] who showed that the quantum theory affords a complete and unambiguous solution of the problem.

At the outset reference may be made to Sommerfeld's equation for the Balmer series of hydrogen given on p. 107, where it was pointed out that the formula has a deepened theoretical significance and its origin has multiple roots. By the admission of elliptical orbits the series has gained no extra lines and has lost none of its sharpness. The significance of this formula has already been dealt with in two directions in Chapter I., but there is yet another important aspect of Sommerfeld's result. In the natural state of the hydrogen atom the various possibilities of generation of emission coincide in one line. If, however, there is imposed an external electric field, the original quantum orbits will be disturbed. It is obvious that the disturbance will affect the various ellipses differently with the result that the energy of these orbits will be altered to a different extent. A qualitative explanation of the Stark effect, therefore, follows at once from Sommerfeld's formula.[3]

[1] *Preuss. Akad. Wiss., Sitzungsber.*, p. 548 (1916).

[2] *Ann. der Phys.*, **50**, 489 (1916).

[3] *Münchener Ber.*, pp. 425 and 459 (1915). This was a preliminary paper in which Sommerfeld only dealt with the problem of plane quantisation. His complete paper, dealt with in Chapters I. and II., was published in *Ann. der Phys.*, **51**, 1 (1916).

This formula, however, is not sufficient of itself to give a complete quantitative explanation of the phenomenon which must be found in the spatial quantising of the orbits, that is to say, the total quantum number is the sum of three quantum numbers, n_1, n_2, n_3, instead of two, as in Sommerfeld's plane formula. This is quite obvious from the fact that the effect of the external field must depend not only on the shape and size of the electronic orbit (two quantum numbers), but also on the spatial position of the orbit with respect to the lines of force of that field (third quantum number). Under the influence of the external field the original orbits are no longer circular and elliptical but become more complicated curves, and the problem is to select from the total number of orbits which are mechanically possible those which are possible or most probable on the quantum theory by choosing three quantum numbers, n_1, n_2, n_3, and expressing the energy of the orbits as functions of those numbers. Each triplet of quantum numbers, n_1, n_2, n_3, in the initial and final orbits gives rise to a different component in the Stark effect, and the increase in the number of these components with the order number of the line in the Balmer series becomes evident. As the total quantum number $(n_1 + n_2 + n_3)$ of the initial orbit increases, the number of quantum triplets into which this number can be resolved also increases, with the result that the number of components in the Stark effect increases.

Epstein dealt with the simple case of a hydrogen-like atom which consists of a single nucleus and a single electron, and applied the Sommerfeld quantum law

$$\int p_i dq_i = nh$$

to a system with three degrees of freedom, each of these being quantised. There is no need to give the details of his treatment, but mention may be made of the choice of co-ordinates. Sommerfeld [1] gives in his book an excellent description of Epstein's treatment and, in reference to the choice of co-ordinates, says that the problem to be considered is the motion of a point mass under the influence of two arbitrary and arbitrarily-placed, fixed (Newton-Coulomb) centres of attraction. The appropriate co-ordinates for this general problem are (according to Jacobi) the parameters of the families of confocal ellipses and hyperbolæ which are described about the two centres as foci, together with the angle measured from the line connecting the centres. The general problem reduces to the special one to be considered, if one of the centres is removed to infinity, whilst its attractive power correspondingly increases. The systems of confocal ellipses and hyperbolæ then resolve into two families of confocal parabolas, of which the second fixed centre, the nucleus, is the focus, and the field direction through it is the common axis.

The important value to be calculated is the energy of the electron,

[1] *Atombau und Spektrallinien*, 4te Auflage, p. 356.

and Epstein showed that, if his expressions for this energy be developed in increasing powers of the intensity of the field F and higher powers than the first be neglected, the energy is given by

$$W = -\frac{2\pi^2 me^4}{h^2}\cdot\frac{1}{(n_1+n_2+n_3)} + \frac{3h^2F}{8\pi^2 me}(n_2-n_1)(n_1+n_2+n_3), \quad (1)$$

where the symbols have the same meaning as on p. 106. In this expression the first term on the right-hand side gives the energy of the electron in the absence of the field, and this may be written in the form

$$W_0 = -\frac{2\pi^2 me^4}{h^2 n^2} = -\frac{Nhx^2}{n^2}, \quad . \quad . \quad . \quad (2)$$

where $n = n_1 + n_2 + n_3$, that is to say, n is the total quantum number. Sommerfeld points out that the same value for the energy is obtained when the Kepler motion is quantised in polar co-ordinates in the limiting case when the external field is zero, which was briefly discussed on p. 316. We see, therefore, that in spite of the difference in paths the energy is the same, provided that the total quantum number is the same ($n_1 + n_2 + n_3 = n$).

The second term on the right side of (1) expresses the change of energy caused by the electric field, and so we may write

$$\Delta W = -\frac{3h^2F}{8\pi^2 me}(n_2-n_1)(n_1+n_2+n_3) \quad . \quad . \quad (3)$$

In order to find the resolution of the lines in the presence of the field we apply the Bohr frequency condition

$$h\Delta\nu = \Delta W_1 - \Delta W_2 \quad . \quad . \quad . \quad . \quad (4)$$

where ΔW_1 is the energy change of the initial state and ΔW_2 that of the final state. If, now, we put n_1, n_2, n_3 for the quantum numbers of the final state, and k_1, k_2, k_3 for the quantum numbers of the initial state, we have

$$\left.\begin{aligned}\Delta\nu &= \frac{3hF}{8\pi^2 me}[(n_2-n_1)(n_1+n_2+n_3) - (k_2-k_1)(k_1+k_2+k_3)]\\ \text{or in wave-numbers}\\ \Delta\nu &= \frac{3hF}{8\pi^2 mev}[(n_2-n_1)(n_1+n_2+n_3) - (k_2-k_1)(k_1+k_2+k_3)]\end{aligned}\right\} \quad (5)$$

where v is the velocity of light.

This is the final formula for the Stark effect with atoms of the hydrogen type, and it expresses the whole of the experimental results obtained by Stark in the case of hydrogen, provided that we apply the selection principle and the rule of polarisation (see p. 110). In applying this formula it must be noted that the quantum numbers n_1 and n_2 may assume the values 0, 1, 2, etc., whilst the quantum

number n_3 may only assume the values 1, 2, etc., the zero value being in this case excluded.

As was stated on p. 110, the selection principle and the rule of polarisation were enunciated in 1918, and were therefore unknown to Epstein at the time his theory was published. In applying the rule of polarisation, it is to be noted that this is only concerned with the quantum number n_3 and by the principle of selection we have

$$k_3 - n_3 = \pm 1 \text{ or } 0.$$

The rule of polarisation states that, in an external field, if

$$k_3 = n_3 \pm 1$$

a wave is emitted which is circularly polarised with respect to the lines of force. When viewed transversely the components due to these transitions will appear polarised at right angles to the lines of force in the sense defined on p. 418. It might be expected that these components would be circularly polarised when viewed longitudinally, and this would be the case if only one process of emission were taking place. In actual fact, in the case of the hydrogen atom each component owes its origin to two sets of emission, which are equal in number and which give rise to left- and right-circular polarisation respectively. When viewed longitudinally, therefore, these components appear unpolarised.

On the other hand, if

$$k_3 = n_3$$

the direction of vibration coincides with the direction of the lines of force, with the result that when the components which have their origin in this transition are viewed transversely, they will be polarised parallel to the lines of force. When viewed longitudinally, these components will be invisible, since no emission takes place in the direction of vibration. These deductions agree with the observations Nos. 3 and 4 given above.

Turning once again to equation (5) it is obvious that observations 7 and 8 at once find their explanation. Thus all the resolutions of lines, that is to say, their separations $\Delta\nu$ from the original position of the line $\Delta\nu = 0$, are integral multiples of a smallest wave-number interval—

$$\Delta\nu = C = \frac{3hF}{8\pi^2 mcv} \quad . \quad . \quad . \quad . \quad (6)$$

Further, this smallest wave-number interval, and consequently the whole structure of a single resolved Balmer line, are magnified proportionally to the strength of the field F.

In the second place, the symmetry of distribution and polarisation of the components with respect to the central undisturbed line is expressed by (5). It is obvious that if a particular transition

$$k_1 k_2 k_3 \rightarrow n_1 n_2 n_3$$

is allowed by the selection principle, there is also possible the transition

$$k_2k_1k_3 \rightarrow n_2n_1n_3.$$

These two transitions will give the same values of $\Delta\nu$, but in the one case $\Delta\nu$ will be positive and in the other it will be negative. This is due to the factor $n_2 - n_1$ which is present in (5). Two components will therefore be obtained, symmetrically distributed with respect to the central undisturbed line. Since the polarisation is determined only by the transition $k_3 \rightarrow n_3$, the polarisation of the two components will be identical.

We are indebted to Sommerfeld [1] for the application of Epstein's equation to Stark's detailed observations of the resolution pictures of the four hydrogen lines under the restrictions set by the selection principle and the rule of polarisation. He shows that the agreement between the number of components calculated from (5) and the number actually observed is truly remarkable, and we may follow his arguments in detail. It is convenient in calculating the number and separation of the components to use the following abbreviations :—

$$K = (k_2 - k_1)(k_1 + k_2 + k_3), \quad N = (n_2 - n_1)(n_1 + n_2 + n_3),$$

$$D = \frac{\Delta\nu}{C} = N - K,$$

that is to say, D represents the displacement, measured in terms of the smallest line-interval C of the component from the original line. What we have to do is to consider all the possible transitions ($k_1k_2k_3 \rightarrow n_1n_2n_3$) subject to the limitations set by the total quantum numbers of the orbits, that is to say, the Bohr quantum numbers, and by the restriction that neither k_3 nor n_3 can have the value zero. It is convenient to subdivide the total number of transitions into the two groups in which $k_3 = n_3$ (p-components) and $k_3 = n_3 \pm 1$ (s-components), respectively.

The general formula for the Balmer series, as was shown in Chapter I. is

$$\nu = N\left(\frac{1}{2^2} - \frac{1}{n^2}\right),$$

where $n = 3$, 4, 5, and 6 for the first four lines. It follows that in each line $n_1 + n_2 + n_3 = 2$, and that $k_1 + k_2 + k_3 = 3$, 4, 5, and 6 for H_α, H_β, H_γ and H_δ, respectively. In the case of H_α we have, therefore,

$$k_1 + k_2 + k_3 = 3, \quad n_1 + n_2 + n_3 = 2,$$

and hence $K = 3(k_2 - k_1)$, $N = 2(n_2 - n_1)$.

Parallel components, $k_3 = n_3$. Here, of course, k_3 cannot have the value 3, since n_3 cannot be larger than 2. Commencing our

[1] *Atombau und Spektrallinien*, p. 370

enumeration, therefore, with $k_3 = n_3 = 2$, there are only two transitions possible, namely,

$$k_1k_2k_3 \rightarrow n_1n_2n_3$$
$$102 \rightarrow 002$$

and

$$012 \rightarrow 002.$$

For the first of these K = − 3 and for the second K = 3, whilst N = 0 in both cases, and we thus obtain two values of D, namely, 3 and − 3 respectively. These two transitions give two components which lie symmetrically with respect to the original line, and since we need only enumerate the transitions which give positive values of D, the existence of the component with the same negative D being assumed, we tabulate only the first of the two transitions. We next have the case $k_3 = n_3 = 1$, in which there are three transitions which give positive values of D, namely,

$$k_1k_2k_3 \rightarrow n_1n_2n_3$$
$$111 \rightarrow 101$$
$$201 \rightarrow 101$$
$$201 \rightarrow 011$$

The above four transitions are the only ones possible under the specified limits, and these are collected in Table CCVII. :—

TABLE CCVII.

H_α, p-components ($k_3 = n_3$).

$k_1k_2k_3 \rightarrow n_1n_2n_3$	K	N	D
102 → 002	− 3	0	3
111 → 101	0	− 2	2
201 → 101	− 6	− 2	4
201 → 011	− 6	+ 2	8

In the case of the perpendicular components where $k_3 = n_3 \pm 1$, we first take $k_3 = 3$ when there is one transition possible, namely 003 → 002. With $k_3 = 2$ there are two transitions, 102 → 101, and 102 → 011. With $k_3 = 1$ there are again two transitions, 201 → 002, and 111 → 002. These are set forth in Table CCVIII. :—

TABLE CCVIII.

H_α, s-components ($k_3 = n_3 \pm 1$).

$k_1k_2k_3 \rightarrow n_1n_2n_3$	K	N	D
003 → 002	0	0	0
102 → 101	− 3	− 2	1
102 → 011	− 3	+ 2	5
201 → 002	− 6	0	6
111 → 002	0	0	0

The central line of the resolved picture arises, therefore, in two ways, and there are, of course, the same number of components with corresponding negative values of D.

In the diagram of Stark's resolution of the hydrogen lines given in Fig. 45 on p. 432, it will be seen that up to D = 4 observation and calculation agree exactly. The calculated lines for which D = 5, 6, and 8 have not been observed, but this is not a serious objection, for it may well be that the intensities of these theoretical components are so weak that they have escaped observation.[1] Stark's conviction that other components do, in fact, exist has already been mentioned on p. 431.

In turning to the other hydrogen lines H_β, H_γ, and H_δ, it must be noted that the same limitations are set to the value of k_3 as in the case of H_α, this being due to the fact that n_3 can only have the values 2 and 1. In Table CCIX. are given the total number of quantum transitions which are possible, it again being understood that only those giving rise to positive values of D are included. As shown previously the corresponding components having the negative values of D are obtained by transposing the quantum numbers k_1 and k_2.

TABLE CCIX.

$H\beta$, p-components ($k_3 = n_3$).

$k_1k_2k_3 \rightarrow n_1n_2n_3$	K	N	D
202 → 002	− 8	0	8
112 → 002	0	0	0
301 → 011	− 12	+ 2	14
301 → 101	− 12	− 2	10
211 → 011	− 4	+ 2	6
211 → 101	− 4	− 2	2

$H\beta$, s-components ($k_3 = n_3 \pm 1$).

$k_1k_2k_3 \rightarrow n_1n_2n_3$	K	N	D
103 → 002	− 4	0	4
202 → 011	− 8	+ 2	10
202 → 101	− 8	− 2	6
112 → 011	0	+ 2	2
211 → 002	− 4	0	4
301 → 002	− 12	0	12

$H\gamma$, p-components ($k_3 = n_3$).

$k_1k_2k_3 \rightarrow n_1n_2n_3$	K	N	D
302 → 002	− 15	0	15
212 → 002	− 5	0	5
401 → 011	− 20	+ 2	22
401 → 101	− 20	− 2	18
311 → 011	− 10	+ 2	12
311 → 101	− 10	− 2	8
221 → 011	0	+ 2	2

[1] See "Intensities of Spectrum Lines," H. A. Kramers, *Kopenhagener Akademie*, 1919, p. 287.

H_γ, s-components ($k_3 = n_3 \pm 1$).

$k_1k_2k_3 \rightarrow n_1n_2n_3$	K	N	D
203 → 002	− 10	0	10
113 → 002	0	0	0
302 → 011	− 15	+ 2	17
302 → 101	− 15	− 2	13
212 → 011	− 5	+ 2	7
212 → 101	− 5	− 2	3
401 → 002	− 20	0	20
311 → 002	− 10	0	10
221 → 002	0	0	0

$H\delta$, p-components ($k_3 = n_3$).

$k_1k_2k_3 \rightarrow n_1n_2n_3$	K	N	D
402 → 002	− 24	0	24
312 → 002	− 12	0	12
222 → 002	0	0	0
501 → 011	− 30	+ 2	32
501 → 101	− 30	− 2	28
411 → 011	− 18	+ 2	20
411 → 101	− 18	− 2	16
321 → 011	− 6	+ 2	8
321 → 101	− 6	− 2	4

$H\delta$, s-components ($k_3 = n_3 \pm 1$).

$k_1k_2k_3 \rightarrow n_1n_2n_3$	K	N	D
303 → 002	− 18	0	18
213 → 002	− 6	0	6
402 → 011	− 24	+ 2	26
402 → 101	− 24	− 2	22
312 → 011	− 12	+ 2	14
312 → 101	− 12	− 2	10
222 → 011	0	+ 2	2
501 → 002	− 30	0	30
411 → 002	− 18	0	18
321 → 002	− 6	0	6

Reference to Fig. 45 on p. 432 shows that all the theoretical components of H_β have been observed, but there have also been observed amongst the p-components D = 4 as a weak line and D = 12 as a doubtful line, whilst there have been observed amongst the s-components D = 0 as a weak line and D = 8 as doubtful. It is very possible that these discrepancies are unreal or due to a secondary effect.

In the cases of both H_γ and $H\delta$ the agreement between calculation and observation is absolute.

It may also be pointed out that only even multiples of D appear in both H_β and $H\delta$ which is to be expected from the formula, since the two total quantum numbers 4 and 2, 6 and 2 are both integral multiples of 2. Again, the components observed with H_β are partially polarised, whilst the polarisation is complete in the case of the components of the other three lines. This is shown by the theory to be

due to the fact that the values of D in the p- and s-series partly overlap, this not being the case with the other three lines. Further, the distance between the neighbouring components increases in the series $H_\alpha \rightarrow H_\delta$. The interval between successive components is one unit with H_α, two units with H_β, three or four units with H_γ, and four units with H_δ.

In conclusion we may consider Epstein's calculation of the intensity of the field from the smallest wave-length interval observed by Stark with the hydrogen lines. As we have already seen, the smallest wave-number interval is given by

$$C = \frac{3hF}{8\pi^2 mev} = \frac{3hF}{8\pi^2 e^2 v} \cdot \frac{e}{m}.$$

If we put $h = 6{\cdot}5 \times 10^{-27}$, $e/m = 5{\cdot}25 \times 10^{17}$, $e = 4{\cdot}69 \times 10^{-10}$, $v = 3 \times 10^{10}$, then, since one electrostatic unit equals 300 volts,

$$C = 6{\cdot}55 \times 10^{-5} \times F$$

expressed in volts per cm. In order to discuss Stark's measurements this must be expressed in wave-lengths, that is to say,

$$\Delta\lambda = 6{\cdot}55 \times 10^{-5} \times \lambda^2 \times F.$$

Now, in the case of H_γ Stark found the smallest separation to be 2·7 A., which Table CCIX. shows to be twice the fundamental interval. We thus have

$$F = \frac{1{\cdot}35 \times 10^{-9}}{6{\cdot}55 \times 10^{-5} \times (4{\cdot}3405 \times 10^{-5})^2}$$
$$= 109{,}400 \text{ volts per cm.}$$

Again, in the case of H_δ the fundamental interval is 1·2 A., whence we have

$$F = \frac{1{\cdot}2 \times 10^{-9}}{6{\cdot}55 \times 10^{-5} \times (4{\cdot}1017 \times 10^{-5})^2}$$
$$= 108{,}900 \text{ volts per cm.}$$

Not only are these two values of F in excellent agreement, but they also are very near to the value measured by Stark, namely 104,000. The difference between observation and calculation is only 5 per cent., which is small when the accuracy of measurement of the wave-length interval is considered. This agreement, together with the quantitative data as regards the spacing of the components, justifies Sommerfeld's statement that the theory of the Stark effect is one of the most striking achievements of the quantum theory in physics.

In the foregoing brief account of Epstein's explanation of the Stark effect only the terms of the first order have been taken into account, and the difference between these gives values of $\Delta\nu$ which are sufficiently accurate for all ordinary purposes. Epstein also

calculated the second order terms, and we may discuss their magnitude, since Sommerfeld [1] pointed out that their difference explains the shift in position of the central *s*-component of H_γ in very strong fields, which was observed by Takamine and Kokubu, and referred to above on p. 433. Epstein [2] calculated by Sommerfeld's complex integration method the second order wave-number difference, and showed that it is given by

$$\Delta_2\nu = \frac{17}{16}\frac{h^6}{(2\pi)^6 e^6 m^3}[\phi_2(n) - \phi_2(k)]F^2 \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where

$$\phi_2(n) = (n_1 + n_2 + n_3)^6\left[1 - \frac{3}{17}\left(\frac{n_2 - n_1}{n_1 + n_2 + n_3}\right)^2 - \frac{9}{17}\left(\frac{n_3}{n_1 + n_2 + n_3}\right)^2\right],$$

and $\phi_2(k)$ is the same, except for the substitution of the initial k orbits for the final n orbits.

As shown above on p. 465, the central *s*-component of H_γ is given by the two transitions

$$113 \to 002 \text{ and } 221 \to 002.$$

For these the value of the first order difference $\Delta_1\nu = 0$, and consequently we would expect the compound to have the same wave-number as that of the original line. The second order differences, $\phi_2(n) - \phi_2(k)$, on the other hand, for the above transitions are

$$\Delta_2\nu = 2^6(1 - \tfrac{9}{17}) - 5^6(1 - \tfrac{9}{17} \times \tfrac{9}{25}) = -1{\cdot}3 \times 10^4$$

and

$$2^6(1 - \tfrac{9}{17}) - 5^6(1 - \tfrac{9}{17} \times \tfrac{1}{25}) = -1{\cdot}5 \times 10^4,$$

and the mean of the two is $-1{\cdot}4 \times 10^4$.

Now the displacement of the middle component of H_γ observed by Takamine and Kokubu was $+1$ A., and in order to compare the calculated value it must be expressed in wave-lengths. We must therefore multiply the above difference by the factor contained in equation (9) and by λ^2. We thus have

$$\Delta_2\lambda = 8{\cdot}72 \times 10^{-15} \times 1{\cdot}4 \times 10^4 \times \lambda^2 \times F^2,$$

and when $\lambda = 4{\cdot}3 \times 10^{-5}$ cm. and $F = 1{\cdot}3 \times 10^5$ volts per cm. (which was the field strength employed),

$$\Delta_2\lambda = +0{\cdot}4 \text{ A.} \quad . \quad . \quad . \quad . \quad (8)$$

This value is decidedly smaller than the observed value of $+1$ A.

In the same strength of field the separation between the first pair of *s*-components was found by Takamine and Kokubu to be 5·25 A., whereas the first order difference between these two (transition $212 \to 101$) is found from equation (5) to be 4·6 A. The second order correction is eliminated by taking the difference between the two

[1] *Ann. der Phys.*, **65**, 36 (1921). [2] *Ibid.*, **51**, 184 (1916).

components, and consequently it would seem that the field strength was probably $1{\cdot}3 \times 10^5 \times 5{\cdot}25/4{\cdot}6$ volts per cm. The second order effect, therefore, in (8) may be multiplied by $(5{\cdot}25/4{\cdot}6)^2$, since equation (7) contains the term F^2. We thus have for the second order shift of the middle component

$$\Delta_2\lambda = +0{\cdot}5 \text{ A.} \quad . \quad . \quad . \quad . \quad (8a)$$

Professor Takamine, in reply to Professor Sommerfeld, said that a careful re-measurement of his photograph found that the displacement was probably nearer to 0·8 or 0·7 A. than 1·0 A. The still remaining difference between observation and calculation has yet to be explained.

The displacement of the central component towards the longer wave-lengths has also been noted in the case of H_ϵ, and indeed it should occur in all the hydrogen lines for which m is odd, *i.e.* H_α, H_γ, H_ϵ, etc. In the case of H_α, equation (7) shows that the displacement will be very small, 0·02 A., and in the case of H_ϵ. $(7/5)^6 = 7{\cdot}5$ times as great as in H_γ.

It is obvious that the pairs of p- and s-components must also be displaced by an amount which equation (7) shows is of the same order as that of the central component. In view of this Takamine re-determined the distances of the two s-components from the position of the original undisturbed line H_γ and found these to be 4·5 A. and 6·0 A. respectively. The mean of these is 5·25, which is the value used above in the re-calculation of the field strength. The position of the two components is thus quite unsymmetrical with respect to the undisplaced line, and this is due to the fact that both components have been displaced by + 0·75 A.

The second order displacement of these two components is therefore + 0·75 A., and this is equal to the newly observed value of the displacement of the central s-component mentioned above. This agreement is to be expected from equation (7).

It must, of course, not be forgotten that the Doppler effect might cause a shift of the lines. Takamine, however, considers that under his experimental conditions the Doppler effect would not be observed, and, further, the absence of any marked displacement of H_α argues against the presence of any Doppler effect. It would, therefore, seem to be well established that Takamine and Kokubu's observations afford at least a qualitative proof of the correctness of Epstein's formula.

CHAPTER IV.

EMISSION BAND SPECTRA.

In the first three chapters of this volume we have dealt with the spectral phenomena associated with matter in the atomic state, that is to say, the emission or absorption of spectrum lines, which, in the case of any individual element, form members of one or more series. There remain to be considered the spectral phenomena associated with molecules, phenomena which exhibit considerable variety in their manifestation. We have, on the one hand, the two phenomena of emission and absorption spectra which in the case of molecules do not appear to be as closely related as we have already found them to be in the case of elementary atoms. Then again, molecular emission spectra may be subdivided into two classes, namely, the spectra of gaseous molecules and the phenomena of fluorescence and phosphorescence which, in the main, are associated with the liquid and solid states.

The magnitude of the subject makes it impossible to discuss the whole within the confines of a single chapter. The subjects of fluorescence and phosphorescence have already been dealt with in Vol. II., Chapter IV., and there remain molecular emission and absorption spectra. Although the theoretical explanation of the former has been applied to a limited number of cases of the latter it is preferable to discuss the two separately. Absorption spectra have long formed a special field of investigation which has a peculiar interest of its own in view of the close relationship it bears with the phenomena of photo-chemistry and of chemical reaction and reactivity in general.

It is proposed in this chapter to deal solely with the emission spectra of gaseous molecules, and the heading of the chapter is justified by the fact that in general these spectra are of the type known as band spectra. By the term band spectrum is meant a fluted spectrum, or channelled space spectrum, which under greater resolving power is resolved into groups of fine lines. These lines always get closer together towards the long or short wave-lengths, until they run together to a single line, which is called the head. A single band thus consists of a single line or head, from which there start one or more series of lines, which become more and more separated the further they are away from the head. A number of these heads with their attendant series form a single band group, and the complete band spectrum exhibited by a substance may contain several band groups.

Such banded spectra are given by nitrogen and water vapour when excited by the electric discharge under reduced pressure. Many others are known, such, for instance, as the cyanogen bands and the several band spectra of the oxides of carbon.

There is no need to enter into details as to these spectra except as regards their structure. For our knowledge of this structure we are indebted to Deslandres, whose work is of fundamental importance. Just as Balmer's work on the series of hydrogen lines was the foundation of all later work on spectral series, so does Deslandres' work stand in relation to all subsequent investigations of the structure of band spectra. From the consideration of a great number of experimental data of measurement Deslandres was able to formulate two laws which will always be known under his name.[1]

The first fact discovered by Deslandres concerns the lines which spring from a single head, and he showed that these lines form series. Each series is of such a type that the differences in the wave-numbers of consecutive lines form an arithmetical series. More than one such series can proceed from each head and in any one band spectrum originating from one particular substance all the bands resemble one another and comprise the same number of series all arranged in the same way. This is known as Deslandres' first law.

A band spectrum thus consists of repetitions of similar groups of lines, *e.g.* pairs, triplets, quartets, etc., and Deslandres attributes the number and distribution of the lines in the groups to the number and distributions of the atoms in the vibrating molecule. It is to be noted that this regular distribution of the lines may be upset to a small extent by certain irregularities and disturbances.

Turning now to the heads of the bands which together form a group, these again are regularly distributed in a manner similar to the lines in each series. The wave-number differences between successive band heads in each group form an arithmetical series, but the arrangement of the heads is reversed with reference to that of the lines forming each band. If the bands themselves are degraded towards the short wave-lengths, that is to say, if the heads are on the long wave side of the line series, then the heads form sub-groups which are degraded towards the long wave-lengths.

Two further points of interest may be noted: first, that if we examine the successive sub-groups of a band spectrum in the direction in which the bands are degraded, it will be found that usually the number of bands in each sub-group is one less than in the previous sub-group; the second point is that whilst the head of each band is the brightest line in the band, the opposite is the case with the heads of the bands forming one sub-group, since, counting from the opposite end of the spectrum from the one to which the bands are degraded,

[1] *Compt. Rend.*, **100**, 1259 (1885); **103**, 375 (1886); **104**, 972 (1888); **112**, 661 (1891); **134**, 747 (1902); **138**, 317 (1904); *Ann. Chim. Phys.*, **15**, 5 (1888); *Journ. de Phys.*, **10**, 276 (1891).

the first head is the brightest in each sub-group, the second one next brightest, and so on.

The arrangement of the heads in a group of bands, so that they form a series, with successive wave-number differences in arithmetical progression, is known as Deslandres' second law.

We may consider these laws of Deslandres more fully. The several series of lines forming each band are so arranged that the frequency differences between successive lines form an arithmetical series. Deslandres pointed this out first for the band with its head at 3914·6 in the negative pole spectrum of nitrogen, that is to say, the band spectrum emitted by the cathode glow in a vacuum tube containing nitrogen. Such a series of lines can be expressed by a formula of the type

$$\frac{1}{\lambda} = A + bn^2,$$

where n is a series of positive integers, 1, 2, 3, etc.

In the case of the band with its head at 3914·6, it can be very closely expressed by the formula

$$\frac{1}{\lambda} = 255{\cdot}454 + 0{\cdot}0015335(n - 1)^2,$$

as is shown by Table CCX. :—

TABLE CCX.

Number of the lines.	$\frac{1}{\lambda}$ observed.	$\frac{1}{\lambda}$ calculated.	Differences.
0	255·454	255·454	0·000
10	255·578	255·578	0·000
15	255·758	255·755	+ 0·003
23	256·197	256·196	+ 0·001
31	256·832	256·834	− 0·002
39	257·672	257·668	+ 0·004
47	258·692	258·699	− 0·007
55	259·916	259·926	− 0·010
63	261·308	261·349	− 0·041

Kayser and Runge [1] proved this law also in the case of the great cyanogen band at λ = 3883·55 ; they have shown, moreover, that the law is not accurate when the series is exceptionally long, as, for example, in the case of this band. The results are shown in Table CCXI., in which the wave-lengths are given :—

[1] *Abhand. Berl. Akad.* (1889).

TABLE CCXI.

n.	λ observed.	Calculated by Deslandres' formula.	Differences.	Calculated by Kayser and Runge.
0	3883·55	3883·55	0·00	3883·48
10	3882·50	3882·51	− 0·01	3882·10
20	3879·36	3879·41	− 0·05	3879·30
30	3874·16	3874·25	− 0·09	3874·13
40	3866·95	3867·04	− 0·09	3866·96
50	3857·82	3857·82	+ 0·00	3857·83
60	3846·79	3846·61	+ 0·18	3846·81
70	3833·93	3833·44	+ 0·49	3833·95
80	3819·36	3818·35	+ 1·01	3819·37
90	3803·16	3801·40	+ 1·76	3803·17
100	3785·42	3782·63	+ 2·79	3785·43
110	3766·39	3762·10	+ 4·29	3766·36
120	3746·15	3739·87	+ 6·28	3746·11
130	3724·91	3716·00	+ 8·91	3724·90
140	3702·92	3690·56	+ 12·36	3702·97
150	3680·51	3663·62	+ 16·89	3680·58
160	3658·05	3635·25	+ 22·80	3658·05

The formula used for the third column was

$$\frac{1}{\lambda} = 25749{\cdot}6 + 0{\cdot}0687n^2.$$

The figures in the fifth column were obtained by Kayser and Runge with a pure interpolation formula,

$$\frac{1}{\lambda} = a + be^{cn} \sin{(dn)^2}.$$

The Deslandres formula gives excellent results up to the seventieth line, but after that the intervals decrease rapidly in relation to the series.

Deslandres also pointed out that when there are more than one series in a band, these series are identical, and may be obtained one from the other by simple addition or subtraction of a constant; each series differs only in the value of the constant A.

Turning now to the second law of Deslandres, we have exactly the same arrangement of the heads of the bands in a group [1] as in the case of the lines in each band. Each group contains several series of heads of bands; each series is so arranged that the intervals between the frequencies of successive heads form an arithmetical progression, and, further, all the series in each group are exactly similar, and may be obtained one from the other by adding or subtracting a constant. This was first proved by Deslandres in the case of the second group

[1] By a group of bands Deslandres defined the whole set of bands the heads of which form associated series; such groups contain sub-groupings, in which the heads of bands are arranged very similarly to the lines in each band, but in the reversed sense, as already explained.

of the positive nitrogen spectrum (λ 5000 — λ 2800). The heads of bands in one series can, therefore, be expressed by a formula of the same type as in the case of the line series—

$$\frac{I}{\lambda} = C + Bn^2.$$

The five series in the second group of the nitrogen spectrum may be quoted, and are set forth in Table CCXII. :—

TABLE CCXII.

Series 1.	Series 2.	Series 3.	Series 4.	Series 5.	Intervals (calculated).
—	—	—	183·251	201·045	
					14·136
—	—	—	197·360	215·179	
					14·428
—	—	193·162	211·792	229·578	
					14·719
—	188·372	207·770	226·517	244·279	
					15·010
—	203·388	222·787	241·518	259·316	
					15·302
198·776	218·685	238·080	256·837	274·664	
					15·593
214·352	234·256	253·714	272·444	290·247	
					15·885
230·247	250·117	269·587	288·337	306·077	
					16·176
246·374	266·350	285·791	304·492	322·247	
					16·468
262·872	282·831	302·230	320·946	338·707	
					16·759
279·636	299·569	318·990	337·723	355·479	
					17·051
296·664	316·628	336·020	354·772	—	

The mean difference between series 1 and 2 is 19·9307, between series 2 and 3 is 19·419, between series 3 and 4 is 18·7247, and between series 4 and 5 is 17·782.

The differences between the consecutive terms are given in the last column ; they form, as can at once be seen, an arithmetical series. The five series are, therefore, absolutely similarly constituted, and only differ from one another by a constant amount in each case.

Cuthbertson [1] was the first to point out that the first group in the positive spectrum of nitrogen could be arranged in the same way ; he arranged the heads of the bands in thirteen series, some of which contain only two members.

This table may be given on account of the interesting way in which it confirms Deslandres' law (Table CCXIII.) :

[1] *Phil. Mag.*, **3**, 348 (1902).

TABLE CCXIII.

1	2	3	4	5	6	7	8	9	10	11	12	13
150·96												
15·31												
166·27	152·78											
15·02	15·01											
181·29	167·79	154·58										
14·78	14·72	14·73										
196·07	182·51	169·31	156·37									
		14·42	14·43									
		183·73	170·80	158·15								
		14·09	14·11	14·13								
		197·82	184·91	172·28	159·91							
		13·86	13·82	13·83	13·84							
		211·68	198·72	186·11	173·75	161·65						
			13·53		13·51	13·54						
			212·25 (?)		187·26	175·19	163·19					
						13·23	13·46					
						188·42	176·65	164·74				
							12·90	13·34				
							189·55	178·08	179·51			
								12·59	12·27			
								190·67	191·78	180·93		
										11·93		
										192·86	182·32	
											11·63	
											193·95	183·73
												11·29
												195·02

All the bands except 163·19 and 164·74 conform to this scheme very well; one band, 183·73, is used twice. Cuthbertson pointed out that the last member of the thirteenth series, 195·02, is consecutive to the last member of the first series.

Deslandres [1] showed that if fifteen series were adopted in place of the thirteen which Cuthbertson recognises, then the two heads at 163·19 and 164·74 at once conform to the scheme, as well as a new head measured by Thalen at 147·29. Further, it is interesting to note that in addition to the fact that the intervals between the horizontal rows form an arithmetical series, the intervals between the vertical columns also form an arithmetical series, which Deslandres has called the second progression.

Now, it has been shown that both the heads of the bands and the lines in the bands can be expressed by formulæ of the type

$$\frac{1}{\lambda} = A + Bn^2.$$

The two formulæ can be united into one—

$$\frac{1}{\lambda} = Am^2 + Bn^2 + C.$$

Deslandres calculated back by means of this formula to the origins of the five series in the second group of the nitrogen spectrum given above; he then found that the squares of the numbers so obtained formed a series, the intervals between the terms of which formed an arithmetic series. The term C can therefore be replaced by $\sqrt{(}p^2 + \gamma$, where p is a series of integers. Again, the term A is not a constant for all the series; it appears to be a simple function of the parameters n^2 and p^2 which define the originating line of the band. Deslandres thus arrives at the general formula

$$\frac{1}{\lambda} = f(n^2, p^2) \times m^2 + Bn^2 + \phi(p^2),$$

m^2, n^2, p^2 being the squares of successive whole numbers, B a constant, and f and ϕ special functions to be determined. In general the variations of m give the rays of one band, and those of n and p the heads of the different bands. By means of this formula the heads of the bands given by Cuthbertson and set forth in Table CCXIII. can be calculated as follows:

$$\frac{1}{\lambda} = 22785{\cdot}1 - \frac{30{\cdot}319}{8}(2n)^2 + \frac{29{\cdot}363}{8}(2p+1)^2.$$

The agreement between calculated and observed values is very good, as shown in Table CCXIV.:—

[1] *Comptes Rendus*, **134**, 747 (1903).

TABLE CCXIV.

n.	p.	Calculated.	Observed.	Differences.
53	48	14737·3	14729	− 8·3
52	48	16329·0	16319	−10·0
52	47	14919·6	14915	− 4·6
51	47	16481·0	16474	− 7·0
51	46	15100·9	15096	− 4·9
50	46	16632·0	16627	− 5·0
49	46	18132·8	18129	− 3·8
48	46	19603·2	19607	+ 3·8
50	45	15281·3	15278	− 3·3
49	45	16782·1	16779	− 3·1
48	45	18252·5	18251	− 1·5
49	44	15460·8	15458	− 2·8
48	44	16931·2	16391	− 0·2
47	44	18371·9	18373	+ 1·1
46	44	19781·1	19782	+ 0·9
45	44	21760·6	21168	+ 7·4
48	43	15639·2	15637	− 2·2
47	43	17079·4	17080	+ 0·6
46	43	18489·2	18491	+ 1·8
45	43	19868·6	19872	+ 3·4
44	43	21217·8	21225	+ 7·2
47	42	15816·7	15815	− 1·7
46	42	17226·6	17228	+ 1·4
45	42	18606·7	18611	+ 4·3
46	41	15993·5	15991	− 2·3
45	41	17372·8	17375	+ 2·2
44	41	18722·0	18726	+ 4·0
45	40	16168·9	16165	− 3·9
44	40	17518·1	17519	+ 0·9
43	40	18836·9	18842	+ 5·1
43	39	17662·4	17665	+ 2·6
42	39	18950·9	18955	+ 4·1
42	38	17805·8	17808	+ 2·2
41	38	19064·0	19067	+ 3·0
41	37	17948·2	17951	+ 2·8
40	37	19176·1	19178	+ 1·9
40	36	18089·7	18093	+ 3·3
39	36	19287·3	19286	− 1·3
39	35	18230·2	18232	+ 1·8
38	35	19397·5	19395	− 2·5
38	34	18369·8	18373	+ 3·2
37	34	19506·7	19502	− 4·7

Deslandres has also investigated very fully the series of lines in the band with head at $\lambda = 3577$ in the second group of the nitrogen spectrum. He finds that there are six series of lines, one series containing pairs. They can all be expressed by the formula

$$\frac{1}{\lambda} = A\left(m + \frac{p}{q}\right)^2 + C.$$

Thus

Series 1 : $\frac{1}{\lambda} = 27946{\cdot}046 + 0{\cdot}1967023(m + \frac{13}{14})^2,$

and so on.

More recently Deslandres [1] has published the results of further work, and he gives reasons which led him to modify his general formula. In the equation given above

$$\frac{1}{\lambda} = f(n^2, p^2) \times m^2 + \mathrm{B}n^2 + \phi(p^2),$$

he previously believed that $\phi(p^2)$ was sometimes a polynomial of the second degree, and this he now finds to be general. The wave-numbers of the heads of the bands are given by the difference of two terms, each of which represents the sum of the terms of an arithmetical progression. He therefore expressed the heads of the bands by

$$\frac{1}{\lambda} = \frac{\mathrm{B}}{2}(n + \beta)^2 - \frac{\mathrm{C}}{2}(p + \gamma)^2 + \mathrm{K}, \qquad . \qquad . \quad (1)$$

and the lines of the whole band by

$$\frac{1}{\lambda} = \frac{(n^2, p^2)}{2} \times (m + \alpha)^2 + \frac{\mathrm{B}}{2}(n + \beta)^2 - \frac{\mathrm{C}}{2}(p + \gamma)^2 + \mathrm{K} \qquad (2)$$

where B, C, K, α, β, and γ are constants.

Whilst he finds that satisfactory results are obtained by this formula, it is not sufficiently general, since it does not include the limiting cases when the argument of the progressions is zero. The lines then form series of constant frequency difference, a simple structure that is observed in many absorption spectra, such, for instance, as that of sulphur dioxide in the ultra-violet.[2] Moreover, the value of α is not always constant as he first believed. For these reasons he gives an improved formula which expresses all emission and absorption spectra—

$$\frac{1}{\lambda} = \pm\left[\frac{f_1(np)}{2} \times m^2 + f_2(np) \times m\right] + \left[\frac{\mathrm{B}}{2}n^2 + b_1 n\right] - \left[\frac{\mathrm{C}}{2}p^2 + c_1 p\right] \pm \mathrm{K} \qquad (3)$$

where m, n, p have successive integral values, positive and negative, B, C, K, b_1, and c_1 are constants, and f_1 and f_2 are simple functions. The variations in n and p give the heads of the different bands and the variations in m give the lines which compose the band.

A band spectrum is not to be represented by a single formula, but by several formulæ of the type (2), for in general each band comprises several series of lines which form arithmetical progressions. Bands of the same origin have the same number of line series arranged in the same way.

Many bands exhibit an interval in their degraded portion, due to

[1] *Compt. Rend.*, **168**, 861, 1179 (1918); **169**, 593, 745, 1365 (1919).
[2] Baly and Garrett, *Phil. Mag.*, **31**, 505 (1916).

a weak or zero intensity of one or more lines of the series. If the central line of the interval be taken as the line 0, the function $f_1(np)$ becomes constant and may be designated as a_1. This phenomenon of zero intensity will be discussed from the theoretical standpoint in the next section. Deslandres shows that it is possible with his formula to represent all bands in terms of their zero lines, and that it is easier in this way to show the correlation with the infra-red region. Thus the absorption spectrum of oxygen consists of two infra-red bands with centres at $\lambda = 4{\cdot}5\mu$ and $3{\cdot}2\mu$, together with bands in the red and yellow which have been resolved into lines. The lines in each of the latter bands have been arranged by Gyllensköld [1] in four arithmetical series, and Deslandres shows that the 47 lines and the centres of the infra-red bands are expressed by the following formula :—

$$\frac{1}{\lambda} = -\frac{f_1(np)}{2} \times m^2 - 5{\cdot}88m + 1062{\cdot}54n - 14{\cdot}112p^2 + 1447{\cdot}17p,$$

where m varies from 0 to 12, n is 2 and 3 for the infra-red and 11 for the visible, p varies from 1 to 5, and the function f_1 is equal to $0{\cdot}2252 + 0{\cdot}146p$.

In a later paper Deslandres says that in taking the zero line as the origin, one is really using a fictitious line, and that better purpose is served at times by taking as origin a real line which is definitely characteristic of the spectrum. If the line of origin is taken in the most intense band, it becomes easier to compare together band spectra amongst themselves and with those of other elements. The constant K will now represent the frequency of the band maxima, and this at once allows the infra-red bands to be correlated, since at present many of these have not been fully resolved.

In comparing together the frequencies of the maxima in all the band spectra of nitrogen, carbon, and oxygen, both emission and absorption, Deslandres has noted a striking relationship, namely, that all these frequencies seem to be multiples of a single fundamental frequency which, expressed in wave-numbers, has the value 1062·5. The values are given in Table CCXV., where the wave-numbers are expressed as multiples of the fundamental unit d :—

TABLE CCXV.

WAVE-NUMBERS OF BANDS OF MAXIMUM INTENSITY.

Nitrogen.

Infra-red Band	$1075 = d + 12{\cdot}5$	ammonia absorption.
First Positive Group	$9430 = 9d - 132{\cdot}5$	nitrogen emission.
,, ,,	$14990 = 14d + 115$	,, ,,
Second Positive Group	$29666 = 28d - 86$	,, ,,
Negative Group	$25546 = 24d + 46$	,, ,,
1st Cyanogen Group	$17025 = 16d + 25$	cyanogen emission.
2nd ,, ,,	$25743 = 24d + 243$	nitrogen emission.
1st Phosphorescent Group	$32940 = 31d - 2{\cdot}5$	,, ,,
2nd ,, ,,	$39192 = 37d - 120{\cdot}5$	,, ,,
Ammonia	$29755 = 28d + 5$	ammonia ,,

Mean of the squares, 89.

[1] *Acad. Stockholm, Mem.*, **42**, No. 8.

Carbon.

Infra-red Band	$2105 = 2d - 20$	carbon monoxide emission.
,, ,,	$3021 = 3d - 166{\cdot}5$	methane absorption.
,, ,,	$3247 = 3d + 59{\cdot}5$	acetylene ,,
,, ,,	$4250 = 4d + 0$	methane ,,
1st Positive Group	$19355 = 18d + 230$	carbon monoxide emission.
2nd ,, ,,	$19275 = 18d + 150$	,, ,, ,,
3rd ,, ,,	$31905 = 30d + 30$	,, ,, ,,
4th ,, ,,	$53234 = 50d + 109$	,, ,, ,,
,, ,, ,,	$55218 = 52d - 32$	,, ,, ,,
Negative group	$41380 = 39d - 57$	,, ,, ,,

Mean of the squares, 80.

Oxygen.

Infra-red Band	$2125 = 2d + 0$	oxygen absorption.
,, ,,	$2125 = 2d + 0$	water ,,
,, ,,	$3268 = 3d + 80{\cdot}5$	oxygen ,,
,, ,,	$5260 = 5d - 52{\cdot}5$	water ,,
,, ,,	$8570 = 8d + 70$	,, ,,
,, ,,	$10600 = 10d - 25$	,, ,,
Visible Band	$15924 = 15d - 13$	oxygen ,,
Rain Band	$16890 = 16d - 110$	water ,,
Visible Band	$17286 = 16d + 286$	liquid oxygen absorption.
Ozone	$16878 = 16d - 122$	ozone absorption.
Negative Group	$19029 = 18d - 96$	oxygen emission.
Ozone	$30893 = 29d - 83$	ozone absorption.
,,	$31875 = 30d + 0$	,, ,,

Mean of the squares, 70.

Infra-red Bands.

Infra-red Band	$1640 = \frac{3}{2}d - 47{\cdot}5$	water absorption.
,, ,,	$1590 = \frac{3}{2}d - 3{\cdot}5$	ammonia ,,
,, ,,	$698 = \frac{2}{3}d - 10$	water ,,
,, ,,	$723 = \frac{2}{3}d + 15$	acetylene ,,
,, ,,	$1298 = \frac{5}{4}d - 30$	methane ,,
,, ,,	$1322 = \frac{5}{4}d - 6$	acetylene ,,
,, ,,	$781 = \frac{3}{4}d - 16$	ammonia ,,
,, ,,	$854 = \frac{4}{5}d + 4$	,, ,,
,, ,,	$861 = \frac{4}{5}d + 11$	water ,,

In the latter portion of Table CCXV. are given nine infra-red bands for which it is necessary to take fractional parts of the fundamental value 1062·5.

This relationship is similar to that previously found in the case of absorption spectra maxima. It must be remarked, however, that

the differences found are in some cases very great in view of the known accuracy of measurement of emission band spectra.

Then again, the fact that in the case of some infra-red bands it is necessary to express the frequencies in terms of sub-multiples of the constant 1062·5 is not satisfactory, especially as in some cases 1062·5/4 is used, and in others 1062·5/5. This would mean that the true fundamental is 1062·5/20 = 53·1, which is too small to justify any conclusions as to the existence of integral multiples.

The Theory of Band Spectra.—A theoretical interpretation of the Deslandres laws was first given by Schwarzschild [1] on the basis of the energy quantum theory, and this has since been extended and amplified by Heurlinger [2] and by Lenz.[3] In 1912 Bjerrum [4] put forward the view that infra-red absorption bands exhibited by compound molecules are due to the rotations of the molecules, the various lines being due to different rotational states. By applying the quantum theory to the energy of the rotating molecules he found that the frequency difference corresponding to two rotational states is given by

$$\Delta\nu = \frac{h}{2\pi^2 \mathrm{I}},$$

where I is the moment of inertia. This view, however, was developed before Bohr had published his theory.

Schwarzschild started from a similar point of view and considered the rotation of a mass around its centre of gravity. He showed that the kinetic energy is given by

$$\mathrm{E} = \tfrac{1}{2}(\mathrm{F}p^2 + \mathrm{G}r^2),$$

where F is the moment of inertia about the axis of rotation, G is that about an equatorial axis, and p and r are the velocities of rotation. Then, if a_1 and a_2 are the moments of momentum, the quantum conditions of the rotations are given by

$$a_1 = \frac{h}{2\pi} m_1 \quad \text{and} \quad a_2 = \frac{h}{2\pi} m_2,$$

where m_1 and m_2 are integers. The values of the kinetic energy are therefore

$$\mathrm{E} = \frac{h^2}{8\pi^2}\left[\frac{(m_1 + m_2)^2}{\mathrm{F}} + \left(\frac{\mathrm{I}}{\mathrm{G}} - \frac{\mathrm{I}}{\mathrm{F}}\right) m_2{}^2\right].$$

If the moments of inertia are equal to one another and we put F = G = I, then we have for the kinetic energy

$$\mathrm{E} = \frac{h^2}{8\pi^2 \mathrm{I}} m^2, \quad . m = 0, 1, 2, \ldots .$$

[1] *Preuss. Akad. Wiss., Sitzungsber.* (1916), 548.
[2] *Phys. Zeit.*, **20**, 188 (1919); *Zeit. Wiss. Phot.*, **18**, 241 (1919).
[3] *Deutsch. Phys. Ges. Verh.*, **31**, 632 (1919).
[4] *Nernst Festschrift* (1912), 90.

Schwarzschild applied this to band spectra and considered a rotating molecule, the electrons exerting no opposing influence on the rotation. If, then, E_0 is the energy due to the electrons in a particular state of the molecule the total kinetic energy of the system will be

$$E_0 + \frac{h^2}{8\pi^2 I} m^2.$$

The total energy of another molecular state will be given by

$$E_0' + \frac{h^2}{8\pi^2 I} m'^2.$$

By the Bohr theory the frequency of the radiation emitted in the change from one state to the other will be

$$\nu = \frac{E_0 - E_0'}{h} + \frac{h}{8\pi^2 I}(m^2 - m'^2) \quad . \quad . \quad (1)$$

If m has a series of integral values a series of lines degraded towards the violet will be obtained,

$$\nu = A + Bm^2 \quad . \quad . \quad . \quad . \quad (2)$$

If m' varies the series will be degraded towards the red.

This at once gives the physical significance of the Deslandres term Bm^2, since $B = h/8\pi^2 I$, where I is the moment of inertia. It will be noted that Schwarzschild arrived at this very important result by quantising the moment of momentum, whereas Bjerrum quantised the energy of the molecules.

Soon after the publication of Schwarzschild's paper Heurlinger [1] deduced the following general result from the application of the above formula to the case of a diatomic molecule. Each molecular state is characterised by three quantum numbers, m, n, and n_1, where m refers to the rotation of the molecule, n to the linear oscillation of the atoms along the principal axis, and n_1 to the electrons. The energy of a particular state, divided by the Planck constant, can be expressed by $\phi(m, n, n_1)$ and the frequency of the radiation emitted in the change from one molecular state to another will be given by

$$\nu = \phi(m, n, n_1) - \psi(m', n', n_1') ;$$

we have therefore

$$\nu = [\phi(m, n, n_1) - \psi(m, n', n_1')] + [\psi(m, n', n_1') - \psi(m', n', n_1')] \quad (3)$$

According to a general law enunciated by Bohr, the value of the difference in the last bracket approximates to $(m - m')\omega$, where ω is the rotational frequency, if $|m - m'| << m$. Since $m - m'$ can only have the values 0 or $\pm$ 1, there will, in general, result three possible series of lines—

$$\left.\begin{aligned} \nu_1 &= F(m) - f(m - 1) \\ \nu_2 &= F(m) - f(m) \\ \nu_3 &= F(m) - f(m + 1) \end{aligned}\right\} \quad . \quad . \quad . \quad (4)$$

[1] *Dissertation*, Lund, 1918; *Phys. Zeitsch.*, **20**, 188 (1919); *Zeitsch. für Phys.*, **1**, 84 (1920).

Of these either ν_2 or ν_1 and ν_3 may be absent. It follows from (4) that

$$\nu_2(m) - \nu_3(m) = \nu_1(m + 1) - \nu_2(m + 1) \quad . \quad . \quad (5)$$

Heurlinger calls these the P, Q, and R series, specifically identifying the Q series with the transition $\Delta m = 0$.

We are indebted to Kratzer for a series of papers in which he developed the theory of band spectra in a remarkable way. In discussing Kratzer's treatment let us first consider the simplest case of a diatomic molecule consisting of two nuclei, the electronic systems of which have a negligible mass. In speaking of the rotations of a molecule, these take place around an axis which is perpendicular to the line joining the two nuclei, rotation round the central line not being considered from the quantum point of view. At the same time it must be remembered that the two nuclei must exist in a position of equilibrium with respect to one another depending on their mutual repulsion and the electronic attractions. The nuclei may be displaced from their equilibrium position by the effect of collisions or any other cause which results in the gain or loss of energy by the system. In short, we must take into account the fact that the molecule can oscillate as well as rotate, and that both motions can be quantised. This had already been accepted by Heurlinger, the quantum number n in formula (3) being used in this sense.

Kratzer [1] first of all treats the problem on the basis that the oscillation is harmonic and that the two, rotation and oscillation, have no mutual influence, and discusses band spectra in the infra-red. As regards the rotation frequencies due to transitions in the rotational state we have already seen that the energy is given by

$$E = \frac{h^2}{8\pi^2 I} m^2,$$

and that the frequency emitted during the transition from one rotational state to another (no change occurring in the oscillational state) is given by

$$\nu = \frac{h}{8\pi^2 I}(m'^2 - m^2) \quad . \quad . \quad . \quad . \quad (6)$$

where m' is the initial and m the final quantum number. Schwarzschild, however, was unaware of the selection principle, and assumed any change in the value of m to be possible. We now know that the change in the value of m is restricted to $\Delta m = \pm 1$ (the transition $\Delta m = 0$ will be dealt with later). If in (6) we put $m' = m + 1$ for emission spectra we have

$$\left.\begin{aligned} \nu &= \frac{h}{8\pi^2 I}[(m + 1)^2 - m^2] \\ &= B(2m + 1) \end{aligned}\right\} \quad . \quad . \quad . \quad (7)$$

[1] *Zeitsch. für Phys.*, 3, 289 (1920).

If $m' = m - 1$ negative wave-numbers will be obtained and will only be obtained in absorption.

The formula (7) is that expressing a true rotation band spectrum and, as can be seen, it leads to a series of equidistant lines, the separation being given by

$$\Delta\nu = 2B = \frac{h}{4\pi^2 I} \quad . \quad . \quad . \quad . \quad (8)$$

On the assumption that the oscillation or vibration is harmonic, the energy is given by $nh\nu_0$ and the wave-number due to a change in vibrational state is

$$\nu = (n' - n)\nu_0 \quad . \quad . \quad . \quad . \quad (9)$$

where, again, the transition in n is restricted to $\Delta n = \pm 1$.

Kratzer points out that a change in the vibrational state without change in the rotational state is not to be expected, whilst change in the latter only or in both simultaneously is possible. When transition occurs in both the quantum numbers m and n the general formula will be

$$\nu = (n' - n)\nu_0 + \frac{h}{8\pi^2 I}(m'^2 - m^2) \quad . \quad . \quad (10)$$

Owing to the relatively large value of ν_0 it is only possible that $n' = n + 1$, since $n' = n - 1$ will lead to negative wave-numbers. For the same reason we may now put $m' = m \pm 1$, and the formula becomes

$$\nu = \nu_0 + \frac{h}{8\pi^2 I}[(m \pm 1)^2 - m^2]$$

$$= \nu_0 + B(\pm 2m + 1) \quad . \quad . \quad . \quad . \quad (11)$$

To this type of spectrum Kratzer gave the name of rotation-vibration spectrum, and here again the separation of the lines is given by

$$\Delta\nu = 2B.$$

It will be noted that in a pure rotation spectrum formula (7) shows that there will be only one series of equidistant lines, and that we put $m' = m + 1$ in emission spectra, and $m' = m - 1$ in absorption spectra. In a rotation-vibration spectrum, according to (11), there will be two branches, positive and negative, according to whether $m' = m + 1$ or $m - 1$. Rotation spectra are believed to occur in the long wave infra-red ($\lambda = 200\mu - 50\mu$), whilst the rotation-vibration bands occur in the short wave infra-red ($\lambda = 20\mu - 1\mu$).

Kratzer applies his formula (11) to the absorption band of hydrogen chloride, which was very accurately measured by Imes [1] with the help of a grating. The distribution of the individual lines is shown in Fig. 56, in which the percentage of absorption is expressed on the ordinates, and the wave-lengths on the abscissæ. This absorption

[1] *Astrophys. Journ.*, **50**, 251 (1919).

band exhibits two very remarkable characteristics which are also shown by the corresponding absorption bands of HF and HBr which were observed by Imes. The first point to be noted is the pronounced gap in the centre of the band, a phenomenon which had been previously noted by several observers and had led them to believe that this and other similar bands were double. The general structure of the band as regards the distribution of intensities of the sub-groups would seem to indicate that this gap is really the centre of the band.

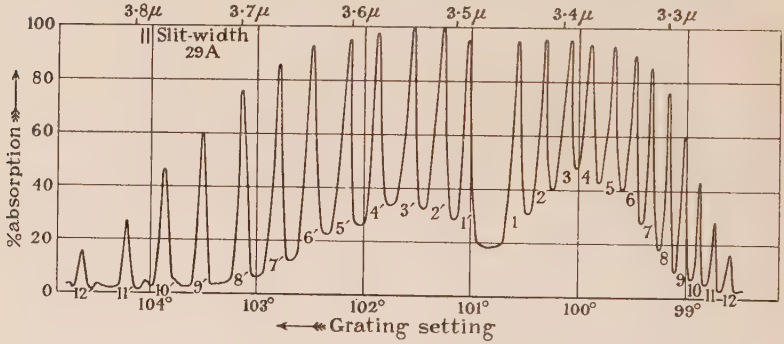


FIG. 56.

We are justified, therefore, in considering that this position of zero intensity is given from (11) by

$$\nu = \nu_0 + B, \quad . \quad . \quad . \quad . \quad (12)$$

that is to say, the position corresponds to the value $m = 0$.

The position thus does not coincide with the nuclear vibration ν_0, but differs from it by one-half of the distance 2B between two consecutive sub-groups. We can, therefore, represent the transitions

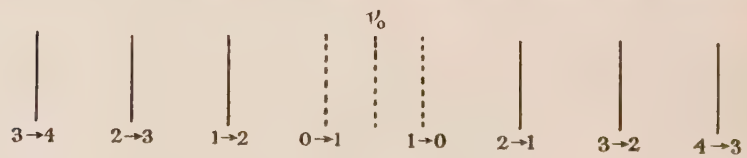


FIG. 57.

in m by the scheme [1] shown in Fig. 57, in which owing to the phenomenon being one of absorption we have $m' = m - 1$.

This, however, raises a difficulty, since the absence of the line at ν_0 indicates that the molecule is in the rotationless state either not at all, or very rarely, or only for a very short period of time. According

[1] This scheme differs from that published by Kratzer in his original paper, and is that given in Sommerfeld's *Atombau und Spektrallinien*, 4te Auflage, Chap. IX., which was written in collaboration with Kratzer.

to Kratzer [1] the difficulty disappears if m is not given integral values 1, 2, 3, etc., but half values $\frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$, etc., and the justification for this need not be discussed here. It must be pointed out that the transitions in m are still integral, that is to say, $m \rightarrow m \pm 1$, the only difference in the Kratzer scheme is that the values of m are not integral, the difference between any two consecutive values of m being ± 1. The transitions of m in the HCl band now become as

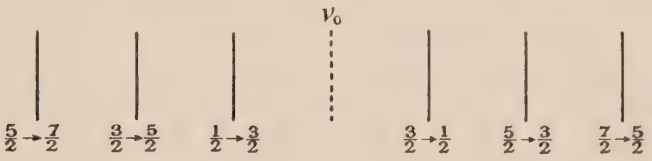


FIG. 58.

shown in Fig. 58. According to this arrangement the zero line is the actual value of ν_0.

The second point of interest in connection with this band is the fact that the frequency difference between the consecutive sub-groups is not a constant (as equation (11) would lead us to expect), but increases towards the longer wave-lengths. The magnitude of this departure from constancy is shown in Table CCXVI., which was given by Imes :—

TABLE CCXVI.

HCl band at 3·46μ.

n.	λ in μ.	ν.	$\Delta\nu$.
12	3·23868	3087·68	12·85
11	3·25224	3074·83	13·27
10	3·26631	3061·56	14·47
9	3·28182	3047·09	15·89
8	3·29903	3031·20	14·92
7	3·31534	3016·28	16·30
6	3·33336	2999·98	17·62
5	3·35305	2982·36	17·38
4	3·37270	2964·98	18·62
3	3·39402	2946·36	18·35
2	3·41529	2928·01	20·24
1	3·43907	2907·77	41·60
1′	3·48897	2866·17	21·75
2′	3·51565	2844·42	22·48
3′	3·54366	2821·94	22·49
4′	3·57214	2799·45	23·04
5′	3·60178	2776·41	23·85
6′	3·63298	2752·56	23·67
7′	3·66450	2728·89	25·30
8′	3·69878	2703·59	25·03
9′	3·73335	2678·56	25·91
10′	3·76982	2652·65	26·15
11′	3·80735	2626·50	26·62
12′	3·84633	2599·88	

[1] *Ann. der Phys.*, **71**, 84 (1923).

In the first column are given the numbers assigned to the sub-groups in Fig. 56, and in the second and third columns are given the wave-lengths and wave-numbers of the sub-groups. The fourth column gives the values of the wave-number difference between each consecutive sub-group, and as can be seen, these increase from 12·85 to 26·62, the total number of sub-groups being twelve on each side of the zero point.

An explanation of this somewhat remarkable phenomenon has been put forward by Kratzer.[1] The formula (11) obtained above was based on a definite assumption which now appears to be incorrect. To briefly re-capitulate, by postulating the existence of molecular rotations and by quantising the moment of momentum we arrived at the expression (7) for the energy difference between any two successive rotational states. By further postulating a nuclear vibration along the axis of figure and by quantising this we arrived at formula (9) for the energy difference between any two successive states. By combining the two together, vibration and rotation, equation (11) was obtained for a rotation-vibration spectrum.

Now it has been assumed that the oscillation of the nuclei is harmonic and that the oscillation and rotation are mutually independent. In his paper Kratzer deals with the problem of the non-harmonic rotating oscillator and the mutual influence of the rotation and oscillation. He shows that as the result of the oscillation the moment of inertia I is not constant, its mean value being different from that of the molecule when oscillation is absent. Furthermore, the rotation changes the strength of the bond between the two nuclei and thus affects their equilibrium position. He denotes the energy of the molecule with rotation quantum m and oscillation quantum n by the symbol W^n_m, the symbol W^n_o referring to the rotationless state. In the case of harmonic oscillation, as we have already seen,

$$W^n_o = nh\nu_0,$$

but when the oscillation is non-harmonic we have to a sufficient approximation

$$W^n_o = nh\nu_0(1 - nx + \ldots), \quad . \quad . \quad . \quad (13)$$

where x is a small constant which depends on the non-harmonic linking of the nuclei. In Sommerfeld's *Atombau und Spektrallinien* (4th edition)[2] Kratzer gives, in a simplified form, the results which he arrives at, and these I venture to give here. The energy of the molecular state represented by W^n_m is given by

$$W^n_m = W^n_o - m^2 n a_n h + \frac{h^2}{8\pi^2 I}(m^2 + \ldots) \quad . \quad . \quad (14)$$

In this expression the coefficient a_n contains the moment of inertia and the force binding the nuclei; it depends on the quantum number

[1] *Zeitsch. für Phys.*, 3, 289 (1920). [2] P. 714.

n and not on the value of m. The third term on the right-hand side of (14) expresses the energy of rotation and has another term involving the products of m^4 into a factor which contains a variation in the moment of inertia.

From (13) and (14) it is easy to recognise the fact that the values of $\Delta\nu$ in a rotation-vibration band should not be constant as was deduced in the harmonic case.

We have

$$\nu=\frac{1}{h}(W^n_{m+1}-W^o_m)=n\nu_0(1-xn+\ldots)-(m\pm 1)^2na_n+B(\pm 2m+1+\ldots)$$

and if m is a sequence of integers with positive and negative values

$$\nu = n\nu_0(1 - xn + \ldots) - (m + 1)^2na_n + B(2m + 1 + \ldots) \quad (15)$$

From this it follows that

$$\Delta\nu = 2B(1 + \ldots) - (2m + 1)na_n \quad . \quad . \quad (16)$$

Instead of being constant, therefore, $\Delta\nu$ is in the first place changed by the centrifugal action of the rotation and in the second place it is progressively decreased, as m increases, by the mutual influence between the rotation and oscillation, the coefficient a_n being positive. Kratzer applies these conclusions with singular success to the absorption bands of hydrogen fluoride, chloride, and bromide.

A further deduction of considerable interest may be made from (13). In the case of harmonic oscillation, transition in the quantum number n of 1 is alone possible, but in the non-harmonic case transitions of 1, 2, 3, etc., may occur. It follows from (13) that the ν_0 in (11) is to be replaced by

$$\nu_0(1 - x), \quad 2\nu_0(1 - 2x), \quad 3\nu_0(1 - 3x) \quad . \quad . \quad (17)$$

In absorption spectra, therefore, where the initial state is $n = 0$, there may be final states where $n = 1, 2, 3$, etc. In emission the final state $n = 0$ and in the initial states $n = 1, 2, 3$, etc. "Overtone" bands are thus rendered possible, and the central wave-numbers of these will not be exact integral multiples of that of the fundamental. The wave-numbers of these overtone bands will be given by (17).

Burmeister [1] measured four rotation-vibration emission bands of HCN, the central frequencies of which Kratzer calculated to be in the ratio

$$1 : 1{\cdot}97 : 2{\cdot}93 : 3{\cdot}91.$$

Since these bands are due to the transitions in n of $1 \to 0$, $2 \to 0$, $3 \to 0$, and $4 \to 0$, it would be expected in the harmonic case that their frequencies would be in the ratio of $1 : 2 : 3 : 4$, even if these transitions were permitted. Kratzer shows that if x in (17) is given the value of $7{\cdot}4 \times 10^{-3}$, then the ratio is obtained

$$0{\cdot}993 : 1{\cdot}960 : 2{\cdot}938 : 3{\cdot}881 = 1 : 1{\cdot}975 : 2{\cdot}95 : 3{\cdot}91,$$

[1] *Dissertation*, Berlin, 1913.

which is extraordinarily close to Burmeister's values. This relation between the central frequencies of the fundamental and overtone bands has been confirmed in certain other cases.

A second important conclusion may be drawn from (16) as regards the value of $\Delta\nu$ in the overtone bands. Equation (16) shows that the value of $\Delta\nu$ changes by an amount which depends principally upon the factor a_n, and it follows that the change in $\Delta\nu$ in the over-

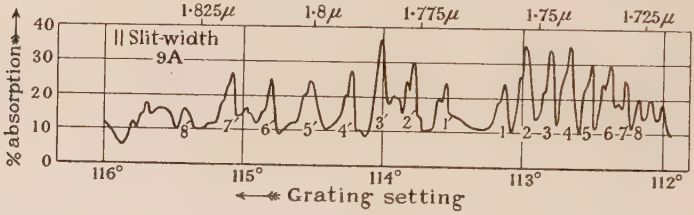


FIG. 59.

tone bands will be greater since a_n depends on the value of n. This conclusion is experimentally supported by Imes' measurements of the sub-groups in the first overtone absorption band of hydrogen chloride at $\lambda = 1{\cdot}76\mu$. In Fig. 59, which is also taken from Imes' paper,[1] is shown the distribution of the sub-groups, the method of plotting being the same as in Fig. 56. The measurements are given in Table CCXVII. :—

TABLE CCXVII.

HCl band at 1·76μ.

n.	λ in μ.	ν.	$\Delta\nu$.
8	1·72711	5790·00	
7	1·73036	5779·15	10·85
6	1·73413	5766·57	12·58
5	1·73844	5752·29	14·28
4	1·74274	5738·11	14·18
3	1·74747	5722·56	15·55
2	1·75255	5705·98	16·58
1	1·75797	5688·40	17·58
1′	1·77015	5646·37	42·03
2′	1·77835	5623·20	23·17
3′	1·78570	5600·04	23·16
4′	1·79329	5576·34	23·70
5′	1·80163	5550·54	25·80
6′	1·80997	5524·96	25·58
7′	1·81874	5498·32	26·64
8′	1·82862	5468·61	29·71

As may be seen from Table CCXVII. the values of $\Delta\nu$ expressed in wave-numbers increase from 10·85 to 29·71, the total number of sub-groups being eight on either side of the zero point.

[1] *Loc. cit.*

Before we pass on to the next section of the general problem of band spectra, reference may be made to a remarkable deduction that was made by Loomis,[1] and also by Kratzer,[2] from Imes' measurements of the infra-red absorption spectra of hydrogen chloride and bromide. In Imes' map of the hydrogen chloride band with centre at $1{\cdot}76\mu$ (shown in Fig. 59), the sub-groups all possess subsidiary maxima on the long wave side which were not included in Table CCXVII. Loomis and Kratzer independently concluded that the two maxima, principal and subsidiary, in each sub-group are due to the existence of the two isotopes of chlorine with atomic weights of 35 and 37.[3] The two maxima are attributed to the nuclear vibrations of the two molecules HCl_{35} and HCl_{37}, respectively, and the agreement between the calculated and observed differences between the wave-lengths of the two maxima is extraordinarily close.

We may represent the relative difference between the nuclear vibration frequencies of HCl_{35} and HCl_{37} by $\delta\nu/\nu$ and the relative wave-length difference as $\delta\lambda/\lambda$, and it may then be shown that

$$d\nu/\nu = \tfrac{1}{2}(\tfrac{1}{35} - \tfrac{1}{37}) = \tfrac{1}{1295},$$

and hence

$$\delta\lambda = -\frac{\delta\nu}{\nu}\lambda = -\frac{1{\cdot}76}{1295} \times 10^{-4}\text{ cm.} = -13{\cdot}54\text{ Ångström.}$$

The negative sign means that the maxima due to HCl_{37} lie on the long wave-length side of the maxima due to HCl_{35}. We know that, since chlorine has the average atomic weight of 35·46, the relative amounts present of HCl_{35} and HCl_{37} must be 3·35 and 1. Consequently the intensity of the maxima due to HCl_{35} must be about 3·35 times the intensity of the maxima due to HCl_{37}.

The observations show that the maxima on the long wave side are decidedly weaker in their relative intensity, and this is just what would be expected. The values of $\delta\lambda$ in Ångströms between the two maxima are given in Table CCXVIII., the numbers given in the first column being those given by Imes to the various maxima.

TABLE CCXVIII.

Sub-group.	δλ.	Sub-group.	δλ.
1	12	1′	14
2	11	2′	16
3	13	3′	—
4	—	4′	10
5	14	5′	9
6	16	6′	22
7	16	7′	—
8	—	8′	—

[1] *Astrophys. Journ.*, **52**, 248 (1920).
[2] *Zeitsch. für Phys.*, **3**, 460 (1920).
[3] F. W. Aston, *Phil. Mag.*, **39**, 611 (1920).

The mean value of $\delta\lambda$ is 14 ± 1 Ångström, and this is extraordinarily close to the calculated value of 13·54 Ångström.

Before the next stage of the theory is developed, namely, the explanation of the visible and ultra-violet bands, attention may be drawn to a point of some interest in connection with rotation-vibration spectra. The quantising of the nuclear vibration referred to an oscillator with a variable electric moment, and this is realised in the case of such molecules as HCl, H_2O, SO_2, etc. On the other hand, in the case of homopolar molecules such as O_2, N_2, H_2, etc., this condition does not obtain, and consequently when their component atoms vibrate in the direction of their axis of figure they lead to no electric moment and hence to no emission or absorption of energy. It follows that in the case of homopolar molecules no rotation-vibration spectra should be exhibited. It is known, for example, that hydrogen and nitrogen exhibit no absorption bands between 100μ and 1μ, which agrees with the above conclusion.

Visible and Ultra-Violet Bands.—We may now turn our attention to the origin of emission of band spectra in the visible and ultra-violet regions, and in applying the foregoing theory it is necessary to consider a third phenomenon in addition to the two already discussed. Reference has already been made to Heurlinger's theory in which a change in the electron configuration was taken into account as well as changes in oscillation and rotation, and the theory was independently developed by Lenz [1] from the theoretical standpoint. Once again are we indebted to Kratzer,[2] who has succeeded in making great advances and in deducing formulæ which give a complete explanation of the structure of certain bands.

One point arises at once in connection with the introduction of changes in the electronic configuration of the nuclei. It was pointed out previously that in the case of a homopolar molecule like N_2 transitions in the oscillation quantum number do not occur, since there is no electric moment. The case is different, however, for such a molecule if one of its constituent atoms is electrically excited by a disturbance of its electronic orbits. The molecule, as a whole, may then acquire an electric moment and therefore become endowed with the power of emitting radiation as an oscillator. It follows that a homopolar molecule may radiate energy due to changes in its oscillation quantum number as well as in its rotation quantum number, provided that there simultaneously occur changes in the electronic configuration of one or other of the two atoms.

We have now to consider the emission of radiation to which there are three contributory causes, and the emission can be expressed by

$$\nu = \nu_e + \nu_n + \nu_m, \quad . \quad . \quad . \quad . \quad (18)$$

[1] *Verh. Deutsch. Phys. Ges.*, **21**, 632 (1919).

[2] *Ann. der Phys.*, **67**, 127 (1922); **71**, 84 (1923); *Zeitsch. für Phys.*, **23**, 298 (1924). See also Sommerfeld's *Atombau und Spektrallinien* (4th ed.), p. 718 *et seq.*

where ν_e represents the contribution due to the quantum jumps in the electron systems, ν_n the contribution due to quantum jumps in the oscillation quantum number n, and ν_m the contribution due to the quantum jumps in the rotation quantum m. The problem is different from that which has previously been discussed, since we now have in the initial and final states two molecules which differ in the configuration of their component atoms or groups of atoms. It is obvious that those constants which depend on the molecular structure will be different in the two states, and these changes must be taken into account.

We may first discuss the contribution ν_m, and in this case the value of the moment of inertia I will be different in the two stationary states which exist before and after the transition in the rotational quantum number m. If the two values of the moment of inertia be I_1 and I we may express the kinetic energy of the initial and final states by

$$\frac{h^2 m_1^2}{8\pi^2 I_1} \quad \text{and} \quad \frac{h^2 m^2}{8\pi^2 I},$$

respectively, in accordance with our previous conclusions. The energy emitted during the transition will be given by

$$h\nu_m = \frac{h^2 m_1^2}{8\pi^2 I_1} - \frac{h^2 m^2}{8\pi^2 I},$$

the frequency being

$$\nu_m = \frac{h m_1^2}{8\pi^2 I_1} - \frac{h m^2}{8\pi^2 I} \quad . \quad . \quad . \quad (19)$$

Applying the principle of selection which limits the transition to $m_1 = m \pm 1$ for the initial state and m for the final state (the transition $\Delta m = 0$ being for the moment neglected), we have

$$\begin{aligned} \nu_m &= \frac{h(m \pm 1)^2}{8\pi^2 I_1} - \frac{h m^2}{8\pi^2 I} \\ &= \frac{h}{8\pi^2 I_1} + \frac{hm}{4\pi^2 I_1} + \frac{hm^2}{8\pi^2}\left(\frac{1}{I_1} - \frac{1}{I}\right) \quad . \quad . \quad . \quad (20) \end{aligned}$$

Introducing this into (18) we have

$$\left.\begin{aligned} \nu = \nu_e + \nu_n + \frac{h}{8\pi^2 I_1} + \frac{hm}{4\pi^2 I_1} + \frac{hm^2}{8\pi^2}\left(\frac{1}{I_1} - \frac{1}{I}\right) \\ = A \pm 2Bm + Cm^2 \end{aligned}\right\} \quad . \quad (21)$$

where

$$A = \nu_e + \nu_n + \frac{h}{8\pi^2 I_1}, \quad B = \frac{h}{8\pi^2 I_1},$$

$$C = \frac{h}{8\pi^2}\left(\frac{1}{I_1} - \frac{1}{I}\right).$$

Equation (21) gives the positive and negative branches of the band spectrum which Heurlinger called the P and R series. As he pointed

out we have also to take into account the transition $\Delta m = 0$ and in this case we have

$$\nu_m = \frac{hm^2}{8\pi^2 I_1} - \frac{hm^2}{8\pi^2 I}$$
$$= \frac{hm^2}{8\pi^2}\left(\frac{1}{I_1} - \frac{1}{I}\right).$$

The formula for this zero branch or, according to Heurlinger, the Q series is therefore

$$\nu = A + Cm^2. \quad . \quad . \quad . \quad . \quad (22)$$

To these three series Kratzer gives the name of partial bands. Sometimes it is found that these series do not consist of single lines, and may be more complex; for example, each member may be a doublet, as Heurlinger found. This is due in all probability to the fact that different values of the term B come into play, and to such systems Kratzer gives the name of associated partial bands.

As was pointed out in the previous section, one of the essential characteristics of emission bands is the running together of the lines to a head. As a matter of fact, Thiele [1] suggested that the head of a band is an accidental accumulation of lines without any specific physical significance, and this is borne out by equation (21). If the wave-numbers of the two branches of lines given by (21) be calculated, it will be seen that this phenomenon of the head of the band finds its explanation. To illustrate this, we may put $2B = 5$ and $C = 0{\cdot}3$ and calculate the values of ν from $\nu = \pm 2Bm + Cm^2$ with $m = -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2}$, etc. The values are given in Table CCXIX.

TABLE CCXIX.

m.	m^2.	$2Bm$.	Cm^2.	Positive branch. $Cm^2 + 2Bm$.	Negative branch. $Cm^2 - 2Bm$.
− 1/2	0·25	− 2·5	0·075	− 2·425	+ 2·575
+ 1/2	0·25	+ 2·5	0·075	+ 2·575	− 2·425
3/2	2·25	7·5	0·675	8·175	− 6·825
5/2	6·25	12·5	1·875	14·375	− 10·625
7/2	12·25	17·5	3·675	21·175	− 13·825
9/2	20·25	22·5	6·075	28·575	− 16·425
11/2	30·25	27·5	9·075	36·575	− 18·425
13/2	42·25	32·5	12·675	45·175	− 19·825
15/2	56·25	37·5	16·875	54·375	− 20·625
17/2	72·25	42·5	21·675	64·175	− 20·825
19/2	90·25	47·5	27·075	74·575	− 20·425
21/2	110·25	52·5	33·075	85·575	− 19·425
23/2	132·25	57·5	39·675	97·175	− 17·825
25/2	156·25	62·5	46·875	109·375	− 15·625
27/2	182·25	67·5	54·675	122·175	− 12·825
29/2	210·25	72·5	63·075	135·575	− 9·425
31/2	240·25	77·5	72·075	149·575	− 5·425
33/2	272·25	82·5	81·675	164·175	− 0·825
35/2	306·25	87·5	91·875	179·375	+ 4·375
37/2	342·25	92·5	102·675	195·175	10·175
39/2	380·25	97·5	114·075	211·575	16·575
41/2	420·25	102·5	126·075	228·575	23·575
43/2	462·25	107·5	138·675	246·175	31·175

[1] *Astrophys. Journ.*, **6**, 65 (1897).

It will be seen at once that the negative branch starts off towards the smaller frequencies and soon turns back on itself towards the larger frequencies. Both branches, when plotted graphically, give a parabola, and with positive values of m the vertex of the parabola of the negative branch lies at $-20{\cdot}825$. If the lines are plotted on a linear scale of wave-numbers it will be seen that those of the negative branch crowd together to the vertex of the parabola, this point forming the "head" of the band, which is thus degraded towards the ultra-violet. This is shown in Fig. 60.

It is evident, therefore, that the enumeration of the lines must not commence from the head of the band, but from the zero line, just as was the case in the two branches of the infra-red absorption band of hydrogen chloride illustrated in Fig. 56 on p. 484. The question arises as to the position of the zero line and the correct enumeration of m on the scale of half-quantum numbers. This question is discussed by Sommerfeld and Kratzer,[1] the latter of whom, as already stated, introduced the conception of half-quantum numbers, and they develop the following argument. If, as in the old method of enumeration, we put $m = 0$ for the line of zero intensity and take integral

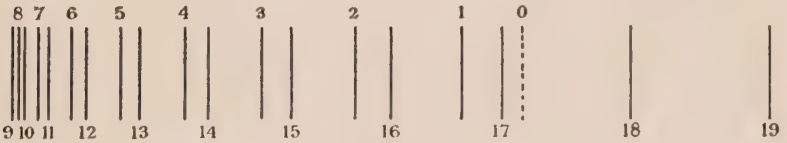


FIG 60.

values of m from $-\infty$ to $+\infty$, we would have for two disturbances the values m_s and $-(m_s + 1)$, and these would correspond to the two transitions $m_s + 1 \rightarrow m$ and $m_s \rightarrow m + 1$. It thus would appear that the disturbances originate in the type of transition rather than in the molecular state, that is, the initial or final state. On the other hand, all the evidence points to the opposite being the case, that is to say, the disturbance must be characteristic of the molecular state and not of the nature of the transition.

This has a very definite influence on the value of m, for, if we assume in the first place that the disturbance is characteristic of the final molecular state, in accordance with the condition that the quantum number indicates the final state, the value for m for both lines must be identical. The enumeration of m must, therefore, be altered by $+\frac{1}{2}$. The two lines due to the disturbance have the quantum numbers $m = \pm(m_s + \frac{1}{2})$. If, on the other hand, the disturbance is characteristic of the initial molecular state, then the enumeration is to be altered by $-\frac{1}{2}$. The zero point now occurs at $m = -\frac{1}{2}$, the disturbances at $m = m_s - \frac{1}{2}$ and $m = -(m_s + \frac{3}{2})$ corresponding

[1] Sommerfeld, *loc. cit.*, p. 722.

to the initial state $m + \frac{1}{2}$. We give, therefore, the following series of values to m :—

$$\ldots -\tfrac{5}{2}, \quad -\tfrac{3}{2}, \quad (-\tfrac{1}{2}), \quad +\tfrac{1}{2}, \quad +\tfrac{3}{2}, \quad +\tfrac{5}{2} \ldots$$

where the bracketed value $(-\frac{1}{2})$ concerns the transition $\frac{1}{2} \rightleftarrows -\frac{1}{2}$ according to whether we attribute it to the positive or negative branch. We may continue to speak of the line which is absent for $m = -\frac{1}{2}$ as the zero line, even though it is no longer attributed to the quantum number $m = 0$.

There remains to be considered the question of the intensity of the lines in these partial bands. In the simple rotation-vibration spectrum, illustrated in Fig. 56 on p. 484 by the infra-red absorption band of hydrogen chloride, it will be seen that the intensity of the component sub-groups rises to a maximum and then falls as the value of the rotational quantum number m increases in the two branches. The two intensity maxima are symmetrically distributed with respect to the central zero line. This clearly means that out of the total number of molecules absorbing energy the greater number undergo the transition in m of $\frac{5}{2} \rightleftarrows \frac{7}{2}$, if the third sub-group counting from the centre have the greatest intensity. The position of the maximum depends on the temperature of the molecules, since the higher is the temperature the greater is the average rotational quantum number. The distribution of intensity obeys the Maxwell-Boltzman law, as Heurlinger [1] showed. The same applies to the two branches of the partial band expressed in (21) and the zero branch expressed in (22).

We may next turn our attention to the band heads and the law connecting these in any band system. In order to do this it is necessary to analyse the contribution denoted by ν_n in equation (18) on p. 490, that is to say, determine the effect of changes in the oscillation quantum number n. This was carried out by Kratzer,[2] who showed that the contribution ν_n is obtained as follows. By (13) on p. 486 the energy of a molecular state defined by the oscillation quantum number n is given to a sufficient degree of approximation by

$$W_0{}^n = nh\nu_0(1 - nx)$$

and consequently the energy of the state characterised by the quantum number n' will be given by

$$W_0{}^{n'} = n'h\nu'_0(1 - n'x'), \qquad . \qquad . \qquad . \qquad (23)$$

where ν'_0 and x' are the new values of ν_0 and x. The frequency contribution is therefore

$$\nu_n = \frac{W_0{}^{n'} - W_0{}^n}{h} = n'\nu'_0(1 - n'x') - n\nu'_0(1 - xn)$$
$$= (n' - n)\nu_0 + n(\nu'_0 - \nu_0) - (n'^2\nu'_0x' - n^2\nu_0x) \qquad (24)$$

[1] *Dissertation*, Lund, 1918; *Zeitsch. für Phys.*, 1, 82 (1920).
[2] *Ann. der Phys.*, 67, 127 (1922).

This value of ν_n must be introduced into the term A of equation (21) above, and we then will obtain the values of the zero lines.

Equation (24) tells us that according to the values of n' and n we obtain a double set of values of A, each of which forms the zero line of a partial band. Furthermore, the three terms are arranged in descending order of magnitude. The first is the largest and depends only on the transition $n' - n$ in the oscillation quantum number. This is termed the group within the band system, the word group being used in a sense different from that used by Deslandres. The second term is smaller, since in general the difference between ν'_0 and ν_0 is small, and depends only on the absolute value of the quantum number. This term gives the single bands which compose each group, these single bands being due to the transitions $\Delta n = 0$, with different absolute values of n. Lastly, the third term gives the deviation from linear progression caused by the non-harmonic oscillation.

The foregoing will be made clearer by reference to a specific case such as the violet band spectrum of "cyanogen." This system consists of four groups with their principal heads at $\lambda = 4606$, 4216, 3883, and 3590. These groups correspond to the transitions

$$n' - n = \Delta n = -2, \ -1, \ 0, \text{ and } +1, \text{ respectively.}$$

Each of these groups consists of five partial bands with the result that each group appears to have five heads. The zero lines of these five partial bands are all due to the same transition $n' \rightarrow n$ as characterises the group to which they belong, and in descending order of wave-length the final quantum numbers (n) are 0, 1, 2, 3, and 4, respectively. For example, the five heads in the first group are at $\lambda = 4606$, 4553, 4515, 4578, and 4532, and as for this group $n' - n = -2$, the five zero lines of these partial bands are given by the transitions

$$2 \rightarrow 0, \ 3 \rightarrow 1, \ 4 \rightarrow 2, \ 5 \rightarrow 3, \ 6 \rightarrow 4.$$

Again, in the 3883 group ($n' - n = 0$) the five zero lines are given by

$$0 \rightarrow 0, \ 1 \rightarrow 1, \ 2 \rightarrow 2, \ 3 \rightarrow 3, \ 4 \rightarrow 4.$$

We are now in a position to derive the complete formula for a band system with one reservation, which applies to the contribution represented by the term ν_e. Too little is at present known about the effect of electron jumps in the atomic nuclei or the properties of a molecule as a whole to justify any attempt to analyse the term ν_e. The equations given above define a single band system with its groups and sets of partial bands. There is little doubt that to the term ν_e we must attribute the existence of more than one band system such as are evidenced, for example, by the red and violet systems of "cyanogen," the positive and negative band systems of nitrogen, etc. This problem has not as yet been solved, and consequently we must, at the present time, leave it in that state.

In deriving the final formula we may, as the first step, introduce the value found for ν_n into the equation (21), whereby we obtain the equation

$$\nu = \nu_e + \frac{h}{8\pi^2 I_1} + n'\nu'_0(1 - n'x') - n\nu_0(1 - xn) \pm 2Bm + Cm^2 \quad (25)$$

It is possible from (25) to obtain a sufficiently accurate expression of the law governing the wave-numbers of the zero lines to enable us to compare it with that deduced by Deslandres for the band heads. As was shown on p. 493, the zero line is given by $m = -\frac{1}{2}$ in the formula for the positive branch of the partial bands and $m = \frac{1}{2}$ in that for the negative branch. The wave-numbers of the zero lines, therefore, are given by

$$\begin{aligned}\nu &= \nu_e + \frac{h}{8\pi^2 I_1} + n'\nu'_0(1 - n'x') - n\nu_0(1 - xn) - B + \frac{C}{4} \\ &= \nu_e + n'\nu'_0(1 - n'x') - n\nu_0(1 - xn) + \frac{C}{4}. \quad . \quad . \quad (26)\end{aligned}$$

Now Delandres, as was stated in equation (1) on p. 477, gave the expression of his law for the band heads in the form

$$\nu = a(n + \beta)^2 - c(p + \gamma)^2 + K$$

whereby

$$\begin{aligned}\nu &= an^2 + 2an\beta + a\beta^2 - (cp^2 + 2cp\gamma + c\gamma^2) + K \\ &= an^2 + bn - (cp^2 + dp) + L.\end{aligned}$$

This agrees with (26) if we put

$$a = -\nu'_0 x', \quad b = \nu'_0, \quad c = -\nu_0 x, \quad d = \nu_0, \quad L = \nu_e + a\beta^2 - c\gamma^2 + \frac{C}{4},$$

and consequently (26) expresses the second law of Deslandres. It must be remembered that (26) refers to the zero lines which are not widely separated from the band heads, so that the Deslandres formula only gives a close approximation to the wave-numbers of the band heads.

In deducing the equations (21) and (25) only the approximate form of the expression (13) was used, and further, the coefficient a_n in (14) involving the moment of inertia and the force binding the nuclei was omitted. Sommerfeld and Kratzer [1] in deriving the complete band formula give the following argument. From a consideration of equation (14) we may obtain an expression for the mutual influence of rotation and oscillation by using

$$\frac{h}{8\pi^2 I} - a_n \text{ in place of } \frac{h}{8\pi^2 I}.$$

[1] Sommerfeld, *loc. cit.*, p. 732.

Now Kratzer, in an application of these formulæ to the cyanogen bands, to be referred to below, found that the term B in (21) is a function of n', and in consequence we substitute the value

$$B(n') = \frac{h}{8\pi^2 I_1} - a'_{n'} \quad . \quad . \quad . \quad (27)$$

Similarly, we write

$$B(n) = \frac{h}{8\pi^2 I} - a_n \quad . \quad . \quad . \quad . \quad (28)$$

and obtain for the term C in (21) the more accurate value

$$C(n',n) = B(n') - B(n) \quad . \quad . \quad . \quad (29)$$

It follows from this that the complete band formula can be written in the form

$$\nu = A(n',\ n) \pm 2B(n')m + C(n',n)m^2 + \ . \quad . \quad (30)$$

where

$$A(n',\ n) = \nu_e + B(n') + n'\nu'_0(1 - n'x') - n\nu_0(1 - nx) + \ . \ . \ .$$

$$B(n') = \frac{h}{8\pi^2 I} - a'_{n'}, \quad B(n) = \frac{h}{8\pi^2 I} - a_n, \quad . \quad . \quad . \quad (31)$$

$$C(n',\ n) = B(n') - B(n).$$

This formula contains three quantum numbers and nine constants.

The foregoing formulæ have been applied with signal success to experimental observations by Heurlinger, Kratzer, and others. It must be noted, however, that even the final equation (30) does not express all the complexities which have been observed in certain cases. This will be understood better from the analysis of the band spectrum of helium which has recently been carried out by Curtis. Before discussing this reference may be made to one or two simple cases which find a very satisfactory explanation by the formulæ deduced above.

One of the neatest of these is that made by Lenz [1] to the fluorescence spectrum of iodine observed by Wood and Kimura.[2] Lenz pointed out that owing to the complexity of the absorption spectrum of iodine it would be a hopeless matter to disentangle the fluorescence spectrum were it excited by white light. Wood, however, succeeded in exciting the fluorescence by monochromatic radiation, using in turn the mercury lines at λ 5462, 5791, and 5770. The question then arises as to the sequence of events under these conditions of excitation. It is obvious that a molecule in a state characterised by the quantum numbers n and m will be brought to an excited state characterised by the quantum numbers n' and m'. Now, owing to the thermal agitation, all possible states of oscillation and rotation will be present, but, since the excitation is monochromatic, only those molecules will be excited which have a definite oscillation quantum

[1] *Phys. Zeitsch.*, **21**, 691 (1920). [2] *Phil. Mag.*, **35**, 236, 252 (1918).

number n and a definite rotational quantum number m. The result of the excitation will be the formation of molecules characterised by the definite quantum numbers m' and n', and these will radiate energy in their transition to a new quantum state. It is very important to note that Wood did not, in general, observe the line series of the partial bands, but pairs of lines with $\Delta\nu =$ constant. Now, by the selection principle the transition in m' is restricted to $m' \rightarrow m \pm 1$, if we exclude the zero branch [see equation (22)] which is also absent in the case of the cyanogen spectrum. Since every excited molecule has the same quantum number m' it follows that the fluorescence emission will consist of a single pair of lines.

The restriction set by the selection principle will naturally break down in cases where the excited molecules collide with one another or with molecules of admixed gases before the emission occurs. Such collisions will result in the appearance of the partial (rotation-vibration) band since the initial and specific value of m' will thereby be changed. Each new value of m' will give rise to a pair of lines, and so the whole partial band will make its appearance. In Wood's experiments the iodine vapour was at room temperature and consequently the collisions taking place between the moments of excitation and emission were relatively few, but with very long exposures he was able to recognise the lines of the partial band symmetrically distributed with respect to the original pair of lines. The relative intensity of the partial band is materially increased when helium or xenon is present, the pressures of the two gases being 4 mm. and 1·25 mm. respectively. As Lenz says, these observations are in exact concordance with the theory.

The theory, therefore, leads to the very facts which Wood observed, namely, pairs of lines of considerable intensity with faint evidences of the remaining lines of the partial bands, all the pairs excited by a single mercury line having the same separation in wave-numbers.

Wood obtained the best results when the iodine vapour was excited by the green mercury line at $\lambda = 5462$, and Wood and Kimura measured twenty pairs of lines with a constant wave-number separation of 5. The measurements are given in Table CCXX. :—

TABLE CCXX.

Order number.	λ.	ν obs.	Δν.	ν calc.	Δν.
0	5462·23 5463·74	18307·5 18302·5	50	18307·5	0
1	5526·55 5528·10	18094·5 18089·4	51	18094·2	+ 0·3
2	Missing.				
3	5658·71 5660·38	17671·9 17666·7	52	17671·5	+ 0·4
4	5726·59 5728·25	17462·4 17457·3	51	17462·1	+ 0·3

Order number.	λ.	ν obs.	Δν.	ν calc.	Δν.
5	5795·79 5797·51	17253·9 17248·8	51	17253·9	0
6	5866·14 5867·85	17046·9 17042·0	49	17047·0	− 0·1
7	Missing.				
8	6010·66 6012·50	16637·1 16632·0	51	16637·0	+ 0·1
9	Missing.				
10	6160·63 6162·48	16232·1 16227·2	49	16632·2	− 0·1
11	6237·68 6239·56	16031·6 16026·8	48	16031·6	0
12	6216·16 6218·14	15832·4 15827·0	50	15832·4	0
13	6396·08 6398·05	15634·6 15629·7	49	15634·4	+ 0·2
14	Missing.				
15	6560·56 6562·68	15242·6 15237·7	49	15242·3	+ 0·3
16	6645·0 6647·0	15048·9 15044·3	46	15048·1	+ 0·8
17	6731·12 6733·28	14856·4 14851·6	48	14855·2	+ 1·2
18	6618·63 6820·01	14665·7 14660·8	49	14663·6	+ 2·1
19	Faint and masked by mercury line.				
20	6998·96 7001·39	14287·8 14282·8	50	14284·2	+ 3·6
21	Missing.				
22	7186·23 7188·68	13915·5 13910·7	48	13909·9	+ 5·6
23	7282·39 7284·92	13731·8 13727·0	48	13724·7	+ 7·1
24	Missing.				
25	7480·4 7482·9	13368·2 13363·8	44	13358·0	+ 10·2
26	Missing.				
27	7685·7 7688·5	13011·0 13006·0	50	12996·4	+ 14·6

The small values of $\Delta\nu$ in Nos. 16 and 25 are undoubtedly due to the fact that these pairs were extremely faint and difficult to measure.

Lenz calculates the value of I from the value $\Delta\nu = 5$ and for this purpose we need only the simple rotational formula $\nu = A + Bm^2$. Since the two lines are due to the transitions $m \rightarrow m+1$ and $m \rightarrow m-1$, the difference in wave-number between them will be

$$\Delta\nu = B(m+1)^2 - B(m-1)^2$$
$$= 4Bm = \frac{mh}{2\pi^2 I}.$$

In order to calculate the value of I it is necessary to know the value of m and to express $\Delta\nu$ in frequency units, *i.e.* $\Delta\nu = 5 \times 3 \times 10^{10}$.

From the position of the doublets in the partial band it is probable that m is about 9. In this way the value of the moment of inertia of the iodine molecule is found to be approximately

$$I = \frac{9 \times 6{\cdot}55 \times 10^{-27}}{2\pi^2 \times 15 \times 10^{10}} = 2 \times 10^{-38} \text{ grm. cm.}^2.$$

This is about fourteen times the value for the nitrogen molecule calculated from the cyanogen bands (see below).

From this value of I the size of the iodine molecule can be obtained, since, if $2l$ be the distance between the two atoms, we have

$$l^2 = \frac{2 \times 10^{-38}}{M_{I_2}},$$

where M_{I_2} is the absolute mass of the molecule. Putting the absolute mass of the hydrogen atom at $1{\cdot}65 \times 10^{-24}$ gram we have

$$l^2 = \frac{2 \times 10^{-38}}{254 \times 1{\cdot}65 \times 10^{-24}},$$

whence $2l = 1{\cdot}36 \times 10^{-8}$ cm., which agrees well with the known molecular magnitude.

Again, the series of line pairs given in Table CCXX. are due to the transitions in the oscillation quantum number n. Wood and Kimura show that the wave-numbers of the more refrangible lines of the pairs are expressed by the formula

$$\nu = 18307{\cdot}5 - 213{\cdot}78\, n + 0{\cdot}637\, n^2,$$

which gives the calculated values in the fifth column of Table CCXX.

If we neglect the refinements due to the term a_n the wave-numbers due to the different values of the oscillation quantum number n can be found to a sufficient approximation from equation (15) to be

$$\nu = n\nu_0(1 - xn)$$
$$= \nu_0 n - x\nu_0 n^2.$$

In the present case the wave-numbers of one of the lines of the pairs is given by

$$\nu = A - \{\nu_0 n - x\nu_0 n^2\}$$

where A is a constant involving ν_e, $\nu_0 = 213{\cdot}8$ and $x\nu_0 = 0{\cdot}637$. It follows, therefore, that the fundamental wave-number of the iodine molecule is 213·8, and the value of x is $2{\cdot}98 \times 10^{-3}$. Apart from the fact that the distribution of the pairs of lines is in accordance with that demanded by the simple Kratzer formula, the fundamental wave-number, as Lenz points out, is in excellent agreement with that calculated from the specific heat. It is also of some interest to note that the value of x is of the same order as that calculated by Kratzer from the HCN bands, namely, $7{\cdot}4 \times 10^{-3}$ (see above, p. 487).

We may next deal with the application by Kratzer of equation (26) to the violet cyanogen band system and his calculation of the wave-numbers of the zero lines.[1] Heurlinger, in his dissertation, observed these with great accuracy so far as the observations went, and gave [2] the following provisional and formal formula : –

$$\nu = 25799{\cdot}75 + f_1(n_1) - (2055{\cdot}64n_2 - 13{\cdot}25n_2^2).$$

Kratzer, in agreement with Heurlinger, attributed the 3884 group to the most frequently occurring oscillation quantum number and the most frequently occurring quantum jump, and he assumed that in this case $n = 0$ and $\Delta n = 0$. On this basis he obtained the following formula for the zero lines of the complete band system :—

$$\nu = 25797{\cdot}83 + 2143{\cdot}88n_1 - 20{\cdot}25n_1^2 - (2055{\cdot}64n_2 - 13{\cdot}25n_2^2)$$

and the resulting values are given in Table CCXXI. :—

TABLE CCXXI.

	$n_2 = 0$.	1.	2.	3.	4.	5.	6.
$n_1 = 0$	(3884) 25797·83 25797·83	(4216) 23755·44 23755·44	(4606) 21739·54 21739·55	—	—	—	—
1	(3590) 27921·3 27921·38	(3872) 25879·0 25878·99	(4197) 23863·0 23863·10	(4578) 21873·4 21873·71	—	—	—
2	—	(3586) 27962·7 27962·04	(3862) 25845·5 25946·15	(4181) 23956·5 23956·76	(4553) — 21993·87	—	—
3	—	—	(3584) — 27989·70	(3855) — 26000·31	(4168) — 24037·42	(4532) — 22101·03	—
4	—	—	—	—	(3850) — 26040·47	(4153) — 24104·08	(4515) — 22194·19

[1] *Ann. der Phys.*, **67**, 127 (1922). [2] *Zeitsch. für Phys.*, **1**, 82 (1920).

In each case the wave-length of the band head is given first, followed by the wave-number of the zero line (where observed) and the calculated wave-number.

In Table CCXXI. the horizontal rows refer to equal values of the initial quantum number, and the vertical columns to equal values of the final quantum number. The diagonal row ($\lambda = 3884$, 3872, 3862, 3855, 3850) corresponds to the quantum transition $n \rightarrow n$, *i.e.* $\Delta n = 0$. The upper diagonal rows proceeding to the right correspond to the groups for which $\Delta n = -1$ and -2, respectively. The lower diagonal row corresponds to $\Delta n = +1$. The constants in (26) have been so chosen as to obtain the best possible agreement with the observed values in the group at $\lambda = 3884$, since the accuracy of measurement is greatest. The differences between calculated and observed values in the remaining groups are very small. Towards the end of the table the observed values of the zero lines are missing, the band heads only having been measured, and consequently at these positions the theory cannot be directly tested.

Kratzer also gives the values of the constants B and C for the partial bands of the violet cyanogen system, and these may be given here. We may, however, quote the more recent values [1] obtained with the half-integral quantum numbers and, indeed, with a later formula involving more terms,[2] and these are set forth in Table CCXXII. :—

TABLE CCXXII.

	$n_2 = 0$.		1.		2.		3.	
	2B.	100C.	2B.	100C.	2B.	100C.	2B.	100C.
$n_1 = 0$	3·919	6·8	3·917	8·6	3·95	10·1	—	—
1	3·92	4·5	3·874	6·4	3·873	8·1	3·92	9·7
2	—	—	3·84	4·1	3·94	5·6	3·86	7·6

As may be seen, the relative values of B and C are in accord with equation (21), since B is proportional to $1/I_1$, whereas C is proportional to $1/I_1 - 1/I$. Furthermore, the values of B do not differ markedly amongst themselves, whilst the values of C on the other hand show considerable variation. This again conforms to (21), since C will evidently be more sensitive than B to changes in the molecule.

The value of the moment of inertia, I_1, can be calculated for the radiating molecule in the same way as was done previously in the

[1] Sommerfeld, *loc. cit.*, 731.

[2] *Akad. Wiss. München, Ber.*, 1922, 107.

case of the iodine molecule, (p. 500). If the value of B in oscillation frequencies is taken as $1{\cdot}96 \times 3 \times 10^{10}$, we have

$$I_1 = \frac{h}{8\pi^2 B} = \frac{6{\cdot}55 \times 10^{-27}}{8\pi^2 \times 5{\cdot}88 \times 10^{10}} = 1{\cdot}41 \times 10^{-39} \text{ grm. cm.}^2.$$

The distance apart of the atoms, assuming that the nitrogen molecule is the origin of the cyanogen spectrum, is given by

$$l^2 = \frac{1{\cdot}41 \times 10^{-39}}{28 \times 1{\cdot}65 \times 10^{-24}} = 3{\cdot}0 \times 10^{-17}, \text{ whence } 2l = 1{\cdot}105 \times 10^{-8} \text{ cm.}$$

The following remarks by Kratzer [1] are of considerable interest in this connection. Heurlinger's formula for the red cyanogen band

$$\nu = 14430 + 1728{\cdot}5n_1 - 13{\cdot}5n_1^2 - (2056{\cdot}0n_2 - 13{\cdot}25n_2^2)$$

shows, as he himself pointed out, that the final state is identical for the red and violet systems. It may also be noted from Heurlinger's formula for the positive band groups of nitrogen that the initial state of the red cyanogen group is the final state of the first positive nitrogen group, and that probably the same is true for the second and fourth positive nitrogen groups. This would indicate that not merely are the two cyanogen band systems radiated by the same molecule, but also that the first, second, and fourth positive band nitrogen groups are to be attributed to the same particle. The question of the origin of the cyanogen bands would thus seem definitely to be answered, namely, that they are due to the N_2 molecule as Runge and Grotrian concluded,[2] since no one will deny that this molecule radiates the positive nitrogen band groups. It is also worthy of note that in all the nitrogen and cyanogen bands the nuclear oscillations are all essentially smaller than the specific heat would lead us to expect. We conclude that none of these bands can be radiated by the unexcited molecule, which agrees with the well-known fact that the solar spectrum shows no nitrogen absorption bands and that nitrogen is completely diactinic to far in the ultra-violet.

So far we have considered one or two simple applications of the band formulæ. When the known examples of band spectra are completely analysed, the relations are found to be more complex than are indicated by our formulæ. The existence of the three series, positive, zero, and negative (Heurlinger's P, Q, and R series), has already been indicated. In general these are found to consist of doublets, the separation of which progressively either increases or decreases as the value of the rotational quantum number m increases. Thus the cyanogen partial bands consist of series of narrow doublets which can only be separated when m is large. The converse is true of the H_2O band at $\lambda = 3064$, where the three series of doublets show decreasing separation as m increases.[3] Again, there occurs the

[1] *Ann. der Phys.*, **67**, 127 (1922). [2] *Phys. Zeitsch.*, **15**, 545 (1914).
[3] Heurlinger, *Dissertation*, Lund, 1918.

phenomenon of displaced series which are well shown by the hydrocarbon band at $\lambda = 4300$, where there are altogether six series of doublets, that is to say, three normal and three displaced series.[1] It is not possible to give a complete account of the work which has been carried out in analysing these various band spectra, but one instance may be selected for detailed consideration, namely, the band spectra of helium. This may be prefaced by a few words on the spectrum of the hydrogen molecule which presents some points of great interest.

The Secondary Spectrum of Hydrogen and the Band Spectrum of Helium.—There is one question which has not been touched on in any way in the preceding pages, and that is the effect of a small value of the moment of inertia, such as is the case with the molecule of hydrogen. The so-called secondary spectrum of hydrogen, that is, the spectrum of the hydrogen molecule, was discussed in Vol. II., Chapter III., but not from the point of view of its structure. The question at once suggests itself as to why the secondary spectrum of hydrogen is not a band spectrum in the ordinarily accepted sense of this term, and it is of considerable interest to seek the answer to this question. It is obvious from what has gone before that the secondary spectrum of hydrogen ought to be a band spectrum and the real question is why the essential characteristics of band structure are not apparent to the eye. When the secondary spectrum is examined it is found that there are no obvious heads of bands, but embryonic partial bands with very few lines have been noted by Fulcher,[2] Gehrcke and Lau,[3] Kiuti,[4] and others.

It is not difficult to see that the whole difference between the appearance of an ordinary band spectrum and that of the secondary hydrogen spectrum is due to the very small value of the moment of inertia of the H_2 molecule. The separation of the lines of a partial band was shown in equation (8) on p. 483 to be

$$\Delta\nu = 2B = \frac{h}{4\pi^2 I},$$

that is to say, the separation is inversely proportional to the moment of inertia. Now, Fulcher showed that the separation of the lines of the partial bands of hydrogen is about 310 in wave-numbers or $9{\cdot}3 \times 10^{12}$ in frequencies. Introducing this value into the above equation we obtain for the moment of inertia of the hydrogen molecule

$$I = \frac{6{\cdot}55 \times 10^{-27}}{4\pi^2 \times 9{\cdot}3 \times 10^{12}} = 1{\cdot}78 \times 10^{-41} \text{ grm. cm.}^2$$

Since this value is very near to the value $2{\cdot}10 \times 10^{-41}$ calculated by Reiche [5] from the specific heat of hydrogen, it follows that the separa-

[1] Kratzer, *Zeitsch. für Phys.*, **23**, 298 (1924).
[2] *Phys. Rev.*, **21**, 375 (1923).
[3] *Akad. Wiss. Berlin, Ber.*, 1922, 453.
[4] *Proc. Math.-Phys. Soc.*, Tokyo, **5**, 9 (1922).
[5] *Ann. der Phys.*, **58**, 682 (1919).

tion observed by Fulcher is very near to that which would be expected from the simple band theory. Our question, therefore, is partly answered in that the consecutive lines of a partial band of the hydrogen molecule will be separated by abnormally large intervals.

There is a second reason for the marked difference between the hydrogen spectrum and an ordinary band spectrum. Sommerfeld and Kratzer [1] point out that in the case of hydrogen the rotational quantum number m cannot have large values. This can well be understood from the probability factor of Boltzmann,

$$e^{-\frac{E}{kT}},$$

where E is the kinetic energy, T the absolute temperature, and k is a constant. On p. 482 it was shown that

$$E = \frac{m^2h^2}{8\pi^2 I},$$

whence we have for the probability factor

$$e^{-\frac{h^2}{8\pi^2 k}\cdot\frac{m^2}{IT}}.$$

It is obvious that the smaller is the product IT, the smaller is the probability of the existence of any but the smallest values of m. Since we have found that I for the hydrogen molecule is very small compared with that for other molecules (I for N_2 is eighty times as large, see p. 503), it follows that large values of m will not exist for the hydrogen molecule, and consequently there will be very few lines in each partial band.

It would thus seem that in the case of the molecular spectrum of hydrogen each partial band will only consist of few lines, and these at large distances apart. Small wonder is it, therefore, that the secondary hydrogen spectrum, although it undoubtedly must conform to the fundamental laws of band spectra, does not present to the eye the characteristic structure we are familiar with in the spectra radiated by heavier molecules. Attention, however, may be drawn to a more recent paper by Kiuti on this spectrum, which will be referred to after the band spectrum of helium has been discussed.

The problem is one of peculiar interest when helium is considered, since under certain conditions of excitation this gas exhibits a spectrum which possesses some of the characteristics of a band spectrum in that band heads are present. The interest lies both in the necessity for postulating the transitory existence of helium molecules and in the intermediate position this spectrum must occupy between the molecular spectrum of hydrogen and the true band spectrum of heavy molecules such as those of nitrogen. The band spectrum of helium was first investigated in 1912 and described in 1913 by Curtis,[2] and

[1] Sommerfeld, *loc. cit.*, p. 737.

[2] *Proc. Roy. Soc.*, **89**, A, 146 (1913).

almost at the same time an independent account was published by Goldstein.[1] This spectrum is developed in the wider parts of the tube when a discharge with small capacity and a small air gap is passed through helium at pressures which are higher than is usual in vacuum tubes containing this gas. The spectrum includes some conspicuous bands with single heads, some with double heads, and a number of complex regions in which no bands are recognisable. One prominent band with head at $\lambda = 5783$ is degraded towards the ultra-violet, whilst all the other bands are degraded towards the red.

An investigation by Fowler [2] led to a remarkable result, since he found that the double heads conform to the criteria of ordinary line series. There are two series of these doublet bands, in which the heads approach one another as the series advance into the ultra-violet. In the case of the main series of doublet bands, the wave-numbers of the less refrangible heads, which are the stronger, can be accurately expressed by the Hicks formula

$$\nu = 34295{\cdot}13 - \frac{109679{\cdot}2}{(m + 0{\cdot}931561 - 0{\cdot}0061/m)^2},$$

the value of N being the earlier value published by Curtis. The second or more refrangible heads are not at all well expressed either by the Rydberg or Hicks formula, so that the two series do not seem to conform to the usual law of a principal series of doublets and to converge to the same limit. The same is true of the second doublet series of bands, for the less refrangible heads are well expressed by a simple Rydberg formula, whilst the more refrangible heads cannot be expressed by the Hicks formula, even with additional constants.

The question of the components of these two series of band heads was discussed by Nicholson,[3] who showed that both component series could be expressed by the generalised Rydberg formula previously used by him.[4] According to Nicholson's view, both component series converge to the same limit. As previously shown, the Nicholson generalisation of the Rydberg formula is of the type

$$\nu = A - N/f(m + \mu)^2$$

where

$$f(m + m) = m + \mu + \alpha/(m + \mu) + \beta/(m + \mu)^2 + \gamma/(m + \mu)^3 \ldots$$

and this formula accurately expresses the second series of doublets. In the case of the first series the coefficients α, β, and γ are alternately positive and negative.

Although this view is not accepted by Curtis, who has made an exhaustive study of the spectrum, the fact is unquestioned that the less refrangible heads in the two doublet series obey the laws of

[1] *Deutsch. Phys. Ges., Verh.*, **15**, 402 (1913).
[2] *Proc. Roy. Soc.*, **91**, A, 208 (1915).
[3] *Ibid.*, **91**, A, 432 (1915).

[4] See p. 62.

ordinary line series. As will be shown presently, the arrangement of the lines in each band conform to the general principles laid down for band spectra. Then again, there is the complex region in which no bands are recognisable. This spectrum, therefore, is of unique interest, since it forms on the one hand a link between the limiting case of band spectra as shown by the secondary spectrum of hydrogen, and on the other hand it forms a link between band spectra and the spectral series of atomic spectra. Not the least interesting fact is that this spectrum must be attributed to the transient existence of a helium molecule. On this point the following remarks of Sommerfeld may be quoted[1]: "We may picture the origin of this helium molecule as follows. Suppose two helium atoms are in an excited state such that one of each of the two electrons of each atom are slightly more distant from the nucleus than usual. Two such helium atoms resemble two hydrogen atoms, for they each consist of an outer electron and an atomic residue having a single positive charge. Thus they are able to enter into a union similar to that of two hydrogen atoms and may, therefore, combine to form an He_2 molecule. Hereby the excitation conditions for hydrogen and helium are opposite. In the case of hydrogen the secondary spectrum arises more readily (at lower potentials) than the Balmer spectrum, in the case of helium, on the other hand, the band spectrum requires a greater excitation than the ordinary series spectra. This seems to me to be quite compatible with the above view, according to which a preliminary condition for the genesis of the helium molecule is a considerable loosening of the helium atoms. The rule that band spectra are to be attributed to molecules and line spectra to atoms is strikingly illustrated by the case of the helium bands. The character of the helium band spectrum compels us to assume the transitory existence of a helium molecule. As this is assumed only for electrical excitation, it by no means contradicts the chemical observations which have to do with unexcited molecules."

To these remarks by Sommerfeld may be added a reference to what was said on p. 238 about the two systems of line series exhibited by helium, which were originally believed to have their origin in two different substances, helium and parhelium. It was there shown that helium could not pass from the metastable state to the normal state by means of a simple transition accompanied by radiation, but only by means of a process analogous to a chemical reaction. It may be that the transitory existence of a helium molecule is connected with this transition from the metastable to the normal state.

The structure of the individual bands of helium has been exhaustively investigated by Curtis,[2] and the conclusions he has reached are of great interest. In the first place, Curtis writes the equations for line series in band spectra somewhat differently from the method

[1] *Atombau und Spektrallinien*, p. 739.
[2] *Proc. Roy. Soc.*, **101**, A, 38 (1922); **103**, A, 315 (1923); **108**, A, 513 (1925).

adopted previously. If the change in the rotational quantum number be $m - 1 \rightarrow m$, then we have

$$\nu = \nu_0 + c_0 - 2c_0 m + c_2 m^2,$$

whilst, from the transition $m \rightarrow m - 1$ we have

$$\nu = \nu_0 - c'_0 + 2c'_0 m + c_2 m^2.$$

Here

$$c_0 = \frac{h}{8\pi^2 I}, \quad c'_0 = \frac{h}{8\pi^2 I_1}, \quad \text{and} \quad c_2 = c_0 - c'_0,$$

I and I_1 being the moments of inertia before and after the quantum jump. As before, we have the zero branch ($m \rightarrow m$) where

$$\nu = \nu_0 + c_2 m^2.$$

Since these three series are usually known as the P, R, and Q series we may adopt the usual abbreviation used in line spectra and write

$$P(m) = \nu_0 + c_0 - 2c_0 m + c_2 m^2$$
$$R(m) = \nu_0 - c'_0 - 2c_0' m + c_2 m^2$$
$$Q(m) = \nu_0 + c_2 m^2.$$

The helium bands contain the three branches, and of these two may at once be identified with the P and Q series, for the values of ν_0 obtained by the use of the above formulæ for the two series are in good agreement. On the other hand, the third series, although it corresponds to the R type as far as its internal structure is concerned, is not correctly situated with respect to the other two, but appears to be shifted bodily through a distance of the order of c'_0. This series, for $m = 0$, extrapolates not to $\nu_0 - c'_0$, as a genuine R series should, but to a value very close to ν_0.

In his work on the band heads of the doublet series referred to above, Fowler showed that the less refrangible heads, which are the Q heads, could be expressed by a Hicks formula, whilst the more refrangible heads could not be so expressed. These latter heads belong to the displaced R or R′ series, and consequently it would seem that Nicholson was incorrect in concluding that the two series of heads behave like a principal series in line spectra. The two heads are essentially different in nature, the Q head marks the termination of a series, whilst the R′ head is merely the turning-point of a series.

When we come to look into the details of the structure of these doublet bands, it is found that they consist in many cases of more than one displaced series. The two bands at $\lambda = 6400$ and 4546 contain P, Q, and R branches as well as a displaced P series. The band at $\lambda = 5730$ includes displaced P and R series and an extra Q series, in addition to normal P, Q, and R series. In every case the lines of the displaced series occur approximately midway between the lines of the normal series.

Now, a great deal of information can be gained by considering the

combination principle. For successive bands of the same series, the final states of the molecule should be the same. If, for example, in the normal P and R branches we consider in any given band the lines $R(m)$ and $P(m+1)$, which are respectively due to the transitions $m \rightarrow (m-1)$ and $m \rightarrow (m+1)$, the initial states are the same and, therefore, the difference $R(m) - P(m+1)$ should be constant for all bands of the same series, since the two final states only are involved. Curtis shows that this difference is actually constant for the same value of m, not only for the P and R branches, but also in the case of $R'(m)$ and $P(m+1)$. This latter fact, which at first appears to be surprising, proves that $R'(m)$ and $P(m+1)$ must have the same initial term. We can, therefore, put

$$\left.\begin{aligned} R'(m) &= \nu_0 + F_1(m) - F_2(m) \\ \text{and} \quad P(m+1) &= \nu_0 + F_1(m) - F'_2(m) \end{aligned}\right\} \quad . \quad . \quad (31a)$$

where the suffixes 1 and 2 refer to the initial and final states respectively. The relation between $F_2(m)$ and $F'_2(m)$ has to be determined, and Curtis shows that this is given by

$$F'_2(m) = F_2(m+1).$$

As regards the form of the functions $F_1(m)$ and $F_2(m)$, Curtis says that, since the wave-numbers can be very nearly represented by a quadratic expression in m, the general formula of Kramers and Pauli [1]

$$F(m) = B(\sqrt{m^2 - \sigma^2} - \epsilon)^2 \quad . \quad . \quad . \quad (32)$$

may be assumed to reduce to the form

$$F(m) = B(m - \epsilon)^2 \quad . \quad . \quad . \quad . \quad (33)$$

where $B = h/8\pi^2 I$, $\sigma h/2\pi$ is the angular momentum of the electrons about the axis of figure, and $\epsilon h/2\pi$ is the angular momentum of the electrons about the perpendicular axis in the plane containing their resultant angular momentum.

We have, therefore,

$$R'(m) - P(m+1) = F_2(m+1) - F_2(m) = 2B_2 m + B_2(1 - 2\epsilon_2) \quad (34)$$

The combination difference is very nearly linear in m, as is required by (34), and may be expressed by the interpolation formula

$$R'(m) - P(m+1) = 15{\cdot}1 + 60{\cdot}783m - 0{\cdot}0500m^2 - 0{\cdot}0333m^3 \quad (35)$$

If we neglect the terms in m^2 and m^3 and compare (35) with (34) we obtain

$$B_2 = 30{\cdot}39 \text{ and } \epsilon_2 = +0{\cdot}2516,$$

and therefore $F_2(m) = 30{\cdot}39(m - \frac{1}{4})^2$ very nearly.

In order to find $F_1(m)$ the final terms are eliminated by forming the differences

$$R'(m) - P(m) = F_1(m) - F_1(m-1) = 2B_1(m) - B_1(1 + 2\epsilon_1) \quad (36)$$

[1] *Zeitsch. für Phys.*, **13**, 351 (1923).

and Curtis shows that the values vary from band to band. Approximate values of the constants were found, for example the interpolation formula for the band at $\lambda = 4650$ was

$$R'(m) - P(m) = -14{\cdot}43 + 57{\cdot}019m - 0{\cdot}0340m^2 - 0{\cdot}02733m^3 \quad (37)$$

From this

$$B_1 = 28{\cdot}51 \text{ and } \epsilon_1 = -0{\cdot}247.$$

We thus arrive at the approximate representation

$$\left.\begin{aligned} R'(m) &= \nu_0 + 28{\cdot}51(m + \tfrac{1}{4})^2 - 30{\cdot}39(m - \tfrac{1}{4})^2 \\ P(m) &= \nu_0 + 28{\cdot}51(m - 1 + \tfrac{1}{4})^2 - 30{\cdot}39(m - \tfrac{1}{4})^2 \end{aligned}\right\} \quad (38)$$

That is to say, the two branches are derived from the same two sets of states, the initial set being characterised by an effective quantum number $(m + \frac{1}{4})$, and the final set by $(m - \frac{1}{4})$. The R′ branch results from a virtual decrease of $\frac{1}{2}$ in the quantum number, and the P branch from an increase of the same amount.

In the case of the Q branch this satisfies no combination principle with the other branches, and hence it must involve a different set of initial states. The close grouping of the lines suggests a transition of the type $(m - \epsilon_1) \rightarrow (m - \epsilon_2)$ where ϵ_1 and ϵ_2 are not very different. It is natural to try the same values of ϵ as before, namely $\pm \frac{1}{4}$. Since no combination relationships exist, ϵ_1 cannot be $-\frac{1}{4}$, and therefore we may try $\epsilon_1 = \epsilon_2 = +\frac{1}{4}$, when the formula becomes

$$Q(m) = \nu_0 + B_1(m - \tfrac{1}{4})^2 - B_2(m - \tfrac{1}{4})^2 \quad . \quad . \quad . \quad (39)$$

Curtis shows that this formula gives a consistent and accurate representation of the series. The three branches may therefore be regarded as arising from the following rotational changes

$$\begin{aligned} R'(m) &\equiv (m + \tfrac{1}{4}) \rightarrow (m - \tfrac{1}{4}) \\ P(m) &\equiv (m + \tfrac{1}{4}) - 1 \rightarrow (m - \tfrac{1}{4}) \\ Q(m) &\equiv (m - \tfrac{1}{4}) \rightarrow (m - \tfrac{1}{4}). \end{aligned}$$

The other transitions, which are possible in addition to these, actually occur in the band at $\lambda = 5730$, and are

$$\begin{aligned} R(m) &\equiv (m - \tfrac{1}{4}) + 1 \rightarrow (m + \tfrac{1}{4}) \\ P'(m) &\equiv (m - \tfrac{1}{4}) \rightarrow (m + \tfrac{1}{4}) \\ Q_2(m) &\equiv (m + \tfrac{1}{4}) \rightarrow (m + \tfrac{1}{4}). \end{aligned}$$

The foregoing has been based on the assumption that the Kramers and Pauli formula degenerates in this case into the form $F(m) = B(m - \epsilon)^2$. This, however, is only an approximation which may hold quite well for small values of m. Kratzer [1] has shown that the complete expression should be of the form

$$F(m) = B(m - \epsilon)^2 - \beta(m - \epsilon)^4 + \quad . \quad . \quad . \quad (40)$$

[1] *Zeitsch. für Phys.*, **16**, 353 (1924).

where $\beta = \frac{4B^3}{\nu_k^2}$, ν_k being the frequency of the nuclear vibrations of vanishingly small amplitude.

Curtis applies (40) to the combination differences $R'(m) - P(m+1)$. From the means of these differences for the bands at $\lambda = 4650$ and $\lambda = 3680$ he obtains by the method of least squares the following interpolation formula :—

$$R'(m) - P(m+1) = 15{\cdot}15 + 60{\cdot}714m - 0{\cdot}0287m^2 - 0{\cdot}03525m^3 \quad (41)$$

and the theoretical expression to which this should be equivalent is

$$R'(m) - P(m+1) = B(1-2\epsilon) - \beta(1 - 4\epsilon + 6\epsilon^2 - 4\epsilon^3) + 2[B - 2\beta(1 - 3\epsilon + 3\epsilon^2)]m - 6\beta(1-2\epsilon)m^2 - 4\beta m^3 \quad (42)$$

From (42) and (41) we obtain

$$B = 30{\cdot}365, \beta = +0{\cdot}00881, \epsilon = +0{\cdot}25052.$$

The value of ϵ is so nearly $\frac{1}{4}$ that $\epsilon = \frac{1}{4}$ exactly was tried, and then by the method of least squares the values of B and β were found to be

$$B = 30{\cdot}3571, \ \beta = 0{\cdot}00883.$$

The final formula

$$F_2(m) = 30{\cdot}3571(m - \tfrac{1}{4})^2 - 0{\cdot}00883(m - \tfrac{1}{4})^4$$

was found to give remarkably close agreement, the differences between observed and calculated values lying between 0·01 and − 0·02. This affords good evidence of the validity of the theoretical formula and the exactness of the $\frac{1}{4}$ value for ϵ.

In the case of the initial R′P terms it has already been pointed out that each band has its own set of initial terms and consequently each band must be treated separately. The final values of the constants are given in Table CCXXIII., from which it can be seen that in four out of six bands ϵ is definitely less than $\frac{1}{4}$.

In the case of the initial Q terms the problem is somewhat different. It was shown above that in all probability the final terms are identical with those of the R′ and P branches, and this view seems to be confirmed by the fact that all the Q branches can be well represented by employing the same final terms as before. We write, therefore,

$$Q(m) = \nu_0 + B(m - \epsilon)^2 - \beta(m - \epsilon)^4 - F_2(m),$$

and by the use of the values obtained by $F_2(m)$ the four constants can be evaluated. The value of ϵ is then so near to $\frac{1}{4}$ that it is evidently necessary to try $\epsilon = \frac{1}{4}$ and the values obtained in this way by the method of least squares are given in Table CCXXIV.

The term ν_0 which originates in a change of electronic and perhaps also nuclear energy was eliminated in the process of determining $F_1(m)$ and $F_2(m)$, but now that we know these it can be calculated from the wave-number of any R′ or P line, thus

$$\nu_0 = R'(m) - F_1(m) + F_2(m) = P(m) - F_1(m-1) + F_2(m).$$

TABLE CCXXIII.

Band.	B.	β.	ϵ_1	(O − C) × 100, R′(m) − P(m).							
				2.	3.	4.	5.	6.	7.	8.	m.
λ4650	28·4100	+ 0·00801	¼	0	+ 2	− 1	+ 1	− 2	0	+ 3	
3680	27·8691	0·00717	¼	− 2	− 77*	+ 135*	+ 1	0	+ 2	− 2	
3350	27·7792	0·00744	0·21707	+ 174*	− 5	+ 11	− 7	—	—	+ 1	
3200	26·8906	0·00690	0·22896	0	0	0	—	—	—	-	
3120	26·553	(0·0065)	0·2041	0	0	—	—	—	—	—	
3070	26·587	(0·00655)	0·1391	0	0	—	-	-		—	

* Denotes affected by perturbation and therefore not used in determining constants.

TABLE CCXXIV.

Band.	ν_0	B_1.	ϵ_1	β_1.	(O − C) × 100.							
					1.	2.	3.	4.	5.	6.	7.	8.
4650	21507·33	28·69289	¼	0·00824	0	+ 2	− 1	0	− 3	+ 1	+ 2	− 1
3680	27193·05	28·54060	¼	0·00839	+ 9	+ 4	+ 1	− 18	−208*	+ 7	− 4	+ 1
3350	29785·52	28·45537	¼	0·00803	+ 18	− 10	+ 127*	− 13	+ 6	+ 12	− 9	0
3200	31180·04	28·44743	¼	0·00836	+ 3	− 10	+ 20	− 8	− 21	+ 30	− 14	+ 2
3120	32016·88	28·44756	¼	0·00862	+ 12	+ 1	+ 8	− 6	− 9	- 17	+ 12	—
3070	32556·83	28·43244	¼	0·00857	+ 16	− 5	+ 5	− 7	− 13	+ 2	+ 3	—
3036	32926·42	28·4225	¼	0·00944	+ 3	− 17	+ 24	− 14	+ 4	—	—	—
3012	33189·02	28·5296	¼	0·01471	+ 8	+ 2	− 3	+ 27	− 6	—	—	—

* Perturbed. Neglected in obtaining formulæ.

The values of ν_0 calculated from the Q branches (by the method of least squares from all the lines) were included in Table CCXXIV., but they are repeated in Table CCXXV., which contains the separate values determined from all the R′ and P lines.

These results present several features of interest. In the first place, the systematic decrease in ν_0 with increasing m may be noted in the band of $\lambda = 4650$, the opposite being the case in the bands at $\lambda = 3680$ and $\lambda = 3350$. The data in the other three bands are too few to provide any reliable evidence. In the second place, there is a discrepancy between the two values (Q and R′P) for each band, and this increases rapidly toward the limit of the series. The band at $\lambda = 3350$ gives an enormous value, even though the perturbed values have been entirely neglected. Since this anomaly is reduced by using the perturbed values of R′(1) and P(2), and practically disappears if the Q value of ν_0 is based on the perturbed Q(3) stronger component, it is possible that the apparently perturbed lines are in their normal positions and that the remaining lines are in reality the perturbed ones.

TABLE CCXXV.

VALUES OF ν_0 DERIVED FROM EACH LINE OF MAIN SERIES.

Band λ.		1.	2.	3.	4.	5.	6.	7.	8.	9.	m.
4650	R′	(21507·47)	07·35	07·31	07·25	07·26	07·19	07·14	07·11	(07·27)	
	P		07·35	07·29	07·27	07·24	07·21	07·14	07·08	(07·10)	
	Q	21507·33									
3680	R′	(27193·22)	93·25	(92·54)*	(93·94)	93·91	93·99	94·07	94·10		
	P		93·27	(93·30)	(92·59)*	93·91	93·98	94·05	94·12		
	Q	27193·05									
3350	R′	(29787·43)*	88·98	88·85	89·04	88·97	—	—	90·34	(88·04)	
	P		(87·24)*	88·90	88·93	89·04	(89·06)	(89·58)	90·33	(90·42)	
	Q	29785·52									
3200	R′	(31181·04)	81·27	81·06	81·33	—	(84·59)	(88·79)	(94·72)		
	P		81·27	81·05	81·33	(81·35)	(82·37)	(84·92)	(89·10)		
	Q	31180·04									
3120	R′	32018·79	18·58	18·43	—	—	(28·20)				
	P		18·57	18·44	(18·13)	(19·18)	(22·29)				
	Q	32016·88									
3070	R′	(32560·97)	61·28	61·09	—	—					
	P		61·28	61·09	(61·11)	(62·82)					
	Q	32556·83									

The Q value is derived from all the lines in the branch by the method of least squares. * Denotes perturbed lines. Values in brackets are from lines not used in calculating the terms, *i.e.* they are extrapolated.

It has already been mentioned that Fowler expressed the wave-numbers of the Q heads by a Hicks formula, but it must be remembered that it is ν_0 and not Q(1) which represents the electronic contribution to the radiation. Curtis finds that the values of the Q branches can be expressed by

$$\nu_0 = 34301{\cdot}82 - \frac{109678{\cdot}3}{(m - 0{\cdot}928075 - 0{\cdot}000449/m)^2} \qquad (43)$$

and in Table CCXXVI. are given the errors O — C, the initial terms and the "effective quantum number" $\sqrt{N}\,r$. The agreement is as good as in an ordinary line series.

Although the perturbations of certain lines have been referred to they have up to now been disregarded. As a matter of fact it is not

TABLE CCXXVI.

Band.	O − C.	Initial term.	Effective quantum number.
λ4650	0*	12794·49	2·9278
3680	0*	7108·77	3·9279
3350	+ 0·03	4516·30	4·9280
3200	− 0·69	3121·78	5·9273
3120	+ 0·16	2284·94	6·9282
3070	0*	1744·99	7·9280
3036	+ 0·57	1375·40	8·9299
3012	− 0·06	1112·80	9·9278

Effective quantum number corresponding to common final term 34301·82 = 1·7882.

* Denotes used in derivation of constants.

an infrequent occurrence for a particular line to be sensibly displaced from its theoretical position in a band series. Kratzer has shown that this phenomenon has its origin in the initial term, that is to say, the energised molecule possesses for a certain velocity of rotation a slightly abnormal configuration. In the helium doublet band system now under consideration there are six perturbed lines, the displacement (O — C) being

Band at λ = 3680.		Band at λ = 3350.	
R′(3)	− 1·03	R′(1)	− 1·47
P(4)	− 1·02	P(2)	− 1·66
Q(5)	− 2·08 (stronger)	Q(3)	+ 1·27 (stronger)
	+ 4·43 (weaker)		− 2·27 (weaker)

Since R′(m) and P(m + 1) suffer identical perturbations (which is established by the absence of perturbation in R′(m) − P(m + 1)) it follows that it is the initial term which is affected as is usually the case. Q(m + 2) is also perturbed in each case, but there is no obvious explanation of this, and it may be due to mere coincidence. The resolution of the perturbed Q lines into two components which are displaced in opposite directions is novel, and it is of some interest that the sum of the intensities of the two components is about equal to that of the expected line. Again, the fact that the displacement of the weaker component is about twice that of the stronger indicates that the perturbation is an actual resolution and is, therefore, of a new type.

Curtis remarks that the R′P perturbation is not so simple as it at first sight might appear. It is worthy of remark that the perturbation is not confined to one line, but extends in a lesser degree to several lines in the vicinity of the one most perturbed. This is not the case in the Q branches, and when considered in conjunction with the resolution of the perturbed Q lines it suggests that there may be

some characteristic difference between the two phenomena in the R'P and the Q branches.

I have given a somewhat full account of this work of Curtis on the band spectrum of helium because it seems to be of very great importance. By his investigations we have learned more about the helium molecule than about any other, and in particular the arrangement of the Q bands in an atomic line series gives evidence which will lead to most valuable information about the electron arrangement within the molecule. Curtis discusses his results at some length in his last paper, and in view of the interest which must be aroused by his conclusions no apology is needed for the following excerpts. In the first place, the structure of the bands indicates that the radiating system is a diatomic molecule, since we know that the bands given by the H_2O and similar molecules are more complicated. It may therefore be assumed that two helium nuclei give rise to practically the whole of the mass and moment of inertia of the molecule. The latter may be calculated directly from the values of B already given, since

$$B = \frac{h}{2\pi^2 I v} cm^{-1},$$

where v is the velocity of light. Then, the masses of the nuclei being known, their distance apart follows at once. So much is possible for any molecule, the bands of which are capable of theoretical interpretation. In the case of the helium molecule we have also terms which give some information of the electron orbits. Since the series equation (43) for the Q values of ν_0 contains N = 109678·3, the series is of the arc type, and therefore the He_2 molecule must be electrically neutral, that is to say, there must be four electrons, one of which radiates. An approximate estimate of the dimensions of the orbit of the latter may be obtained in the following way.

The total energy of the electron, if it move in an elliptic orbit of major semi-axis a under the influence of a constant charge E will be $-Ee/2a$, but, owing to the influence of the other three electrons, the effective value of E will not be constant. The orbit will therefore not be truly elliptical, but the simple formula should suffice to determine the order of magnitude of the orbit. The corresponding term

$$\nu = \frac{W}{h},$$

will therefore be approximately proportional to a^{-1}. If a_H represents the radius of the 1_1 orbit for hydrogen, the corresponding term is N, the Rydberg constant. Hence

$$\frac{\nu}{N} = \frac{a_H}{a},$$

and

$$a = \frac{N}{\nu} a_H.$$

In Table CCXXVII. are given the values of the moment of inertia, separations ($2r$) of the nuclei, and a.

TABLE CCXXVII.

Band.	State.	$I \times 10^{-40}$.	$2r$.	a.
4650	Initial $(m + \frac{1}{4})$	0·9718 gm. cm².	0·543 A.	4·54 A.
3680	,, ,,	0·9907 ,,	0·548	8·18
3350	,, ,,	0·9939 ,,	0·549	12·87
3200	,, ,,	1·0268 ,,	0·558	18·62
3120	,, ,,	1·0397 ,,	0·561	25·44
3070	,, ,,	1·0384 ,,	0·561	33·31
All	,, $(m - \frac{1}{4})$	0·9689 ,,	0·542	As for $(m + \frac{1}{4})$
All	Final $(m - \frac{1}{4})$	0·9095 ,,	0·525	1·695

NOTE.—The electron orbits associated with the initial $(m - \frac{1}{4})$ states are practically indistinguishable from the corresponding $(m + \frac{1}{4})$ values.

We cannot determine the azimuthal quantum number of the orbits, but since the " effective quantum numbers " of the final and inmost initial orbits are 1·79 and 2·93 (see Table CCXXVI. on p. 514), the total quantum numbers are probably 2 and 3 respectively. The transitions might therefore be $3_3 - 2_2$ (diffuse), $3_2 - 2_1$ (principal) or $3_1 - 2_2$ (sharp). Some of this uncertainty would disappear if it were known whether a further member exists corresponding to $m = 1$, which would occur at about $\lambda = 2{\cdot}09\mu$. Curtis has commenced a search for helium bands in the infra-red region.

It appears that in the final state the orbit of the radiating electron is nearly seven times larger than the distance between the nuclei, and in the initial state this electron may retire to a much greater distance with comparatively little effect on the nuclear separation. The inference is that the latter is mainly determined by the position of the other three electrons, some, at least, of which are much closer in than the one which radiates, since this appears to be too far distant to play any essential part in the binding of the nuclei. We thus obtain some concrete evidence in favour of the suggestion made on p. 507 as to the formation of the He_2 molecule.

Again, in the initial $(m + \frac{1}{4})$ states the distance apart of the nuclei perceptibly increases as the electrons recede from them, and when the electron comes closer in, as in the final $(m - \frac{1}{4})$ state, the separation decreases. It is remarkable that no such effect exists in the case of the initial $(m - \frac{1}{4})$ states, for here the moment of inertia remains sensibly constant whatever the position of the electron. The only essential difference between the two sets of states $(m \perp \frac{1}{4})$ consists in the sense of the angular momentum of the electrons. At present it is not possible to explain why in the one case and not in the other the position of the radiating electron should affect the size of the

molecule, and it may be that in this may be found an important clue to the structure of the He_2 molecule.

Another point of interest arises over the difference between the values of ν_0 derived from the R′P and Q branches. We may write hW_1^+ and hW_1^- for the initial values of the electronic energy in the $m + \frac{1}{4}$ and the $m - \frac{1}{4}$ states, respectively, and hW_2^+ and hW_2^- for the two final states, since $h\nu_0 = W_1 - W_2$. The complete expressions for the three branches will then be

$$\begin{aligned} R'(m) &= W_1^+ - W_2^- + F_1(m + \tfrac{1}{4}) - F_2(m - \tfrac{1}{4}) \\ P(m) &= W_1^+ - W_2^- + F_1(m - 1 + \tfrac{1}{4}) - F_2(m - \tfrac{1}{4}) \\ Q(m) &= W_1^- - W_2^- + F_1(m - \tfrac{1}{4}) - F_2(m - \tfrac{1}{4}). \end{aligned}$$

The differences between the two values of ν_0 will be given by

$$\nu_0^{R'P} - \nu_0^{Q} = W_1^+ - W_1^-.$$

We saw previously that this is negligible for the inner orbits, but increases with the electronic quantum number. In other words, the two states $(m \pm \frac{1}{4})$ are practically identical when the electron occupies an inner orbit, but they differ appreciably when it moves out. Since this agrees with what has already been found from consideration of the moments of inertia, there is no difficulty in accounting for the two values of ν_0; in fact, the difference between them is surprisingly small.

The frequency ν_0 has been assumed to be entirely electronic in character, but it is possible that it may be partly due to nuclear vibrations. The fundamental frequency of such should be given by $2v\sqrt{B^3/\beta}$, and if this remains the same for different positions of the radiating electron, the values of $\sqrt{B^3/\beta}$ should be the same for all states of the molecule. The actual values of $\nu_k = 2\sqrt{B^3/\beta}$ are as follows:—

Final R′P state		3560 cm.$^{-1}$
Initial Q state (average)		3330
,, R′P state	4650	3380
,, R′P state	3680	3480
,, R′P state	3850	3400
,, R′P state	3200	3360
	Mean	3420 cm.$^{-1}$

The agreement is good; if nuclear vibrations occur we should expect to find bands of similar nature at a distance of about 3400 cm.$^{-1}$ from the bands now under discussion. If such bands exist their intensity must be very small, since no other similar bands have been found anywhere between $\lambda = 7000$ and $\lambda = 2000$.

The bands considered in the foregoing belong to what Curtis calls the main series of doublet bands, and there are four other doublet bands at $\lambda = 5130$, 4000, 3630 and 3460, which he calls the second series. The structure of these is quite analogous to that of the main

series, including the two states ($m \pm \frac{1}{4}$). The only two points worthy of remark here are (1) that the difference between the two values of ν_0 determined from the R′P and Q branches has the opposite sign compared with the difference in the main series, and (2) that the four values of ν_0 from the Q branches can be represented by the formula

$$\nu_0 = 31958{\cdot}14 - \frac{109678{\cdot}3}{(m + 0{\cdot}964366)^2}.$$

An obvious possibility is that this second series is related to the main series in the sense that they differ only in respect of nuclear vibration terms. Against this it can be argued (1) that the difference in the wave-numbers of the corresponding members is not 3400 but about 2000 cm.$^{-1}$, and (2) that the electron terms are considerably different in the two series.

It is quite possible that no nuclear vibration at all can take place and that an unstable molecule such as He_2 can only exist so long as the nuclei are at rest relatively to one another. An approximate calculation, based on the value 3400 cm.$^{-1}$ for the fundamental vibration number and assuming simple harmonic vibrations, indicates for the one-quantum state an amplitude of about one-fifth of the distance between the nuclei. It would not be surprising if an unstable molecule failed to survive such a violent disturbance.

In conclusion, the theory of emission band spectra, since it involves an electron transmission as part of the radiating mechanism, would lead us to expect the occurrence of band head series arranged according to line series laws. As far as our present knowledge extends, the helium bands are the only two groups which fulfil this expectation. We must conclude that there is, in general, an essential difference between the circumstances of electronic emission from atoms and molecules. Whatever the cause, it appears that in the latter case there is no set of stationary electron states, such as occur in the former, or else that, if such exist, their energies are distributed according to a different law. Curtis suggests the following explanation for this. A molecule depends for its existence upon a special configuration of the electrons belonging to the outer shells of the constituent atoms, and it may be impossible to remove one of these electrons without causing the dissociation of the molecule. In other cases the molecule may continue to exist, but with such a different configuration that the energy of the radiating electron differs considerably from the value it would have had if the molecule had remained as before. The two cases correspond to the two possibilities suggested above. Or, again, the energy required to displace an electron may exceed that required to break up the molecule. The atom, on the other hand, is practically unaffected by the position of the radiating electron, which may therefore occupy any one of a series of temporarily stable orbits.

It must be admitted, however, that these considerations are not

entirely valid for a molecule capable of taking up a positive charge, for if, as this implies, it can survive the complete removal of an electron, it would seem reasonable to expect a series of intermediate states comparable with those characteristic of an excited atom, and therefore giving rise to a series of bands arranged after the manner of a line series. This feature of the present bands is no doubt to be attributed to the exceptional constitution of the helium molecule concerned. It is probably formed from two excited helium atoms, so that at least one of the four electrons will be in an "outer" orbit already, and may, in consequence, move still farther out without appreciable effect on the molecule.

An interesting paper on the secondary or band spectrum of hydrogen has recently been published by Kiuti,[1] who describes the excitation of this spectrum by means of the arc discharge between a bundle of tungsten filaments and a block of tungsten or molybdenum in hydrogen at 460 mm. pressure. The spectrum contains many lines of large intensity in the region of longer wave-lengths than 5650 Å., those of shorter wave-length being of feeble intensity.

It was found that between $\lambda = 5950$ and $\lambda = 5800$ there are seven conspicuous lines which seem to obey the parabolic law of arrangement. The wave-lengths of these lines were accurately determined, and these are given in Table CCXXVIII. :—

TABLE CCXXVIII.

m.	λ in I.A.	ν obs. *in vacuo.*	ν calc.	Obs.—Calc.	Remarks.
1	5812·53	17199·45	17199·47	− 0·02	
2	5819·39	17179·17	17179·05	+ 0·12	Broad.
3	5831·00	17144·98	17145·03	− 0·05	
4	5847·28	17097·23	17097·39	− 0·16	
5	5868·21	17036·27	17036·15	+ 0·12	
6	5894·04	16961·60	16961·29	+ 0·31	Complex.
7	5925·02	16872·81	16872·82	− 0·01	

The calculated values are given by the formula

$$\nu = 17206{\cdot}28 - 6{\cdot}8052m^2,$$

the constants being determined by the method of least squares from six of the measurements, $m = 6$ being omitted because this line is probably complex.

This series must thus be the Q series of a complete band, and Kiuti shows that the R and P series are given by the Fulcher bands. Now the green band of these consists of triplets, and if the curves be plotted with ν as abscissa and m as ordinate these three curves intersect the curve of the Q series at the point $m = \frac{1}{2}$. Arguing from

[1] *Nagaoka Anniversary Volume*, p. 193, Tokyo, 1925.

Curtis' results with the helium bands Kiuti concludes that these green bands form the R series. On the other hand, the red Fulcher bands which also contain triplets give a curve which cuts the Q curve very nearly at $m = 0$ and, consequently, these may be taken as the P′ series. The red Fulcher bands also contain four other series which seem to be the P series, since their curve cuts the Q series curve at the point $m = \frac{1}{2}$. The final formulæ given by Kiuti are

$$\text{P series } \nu = 17338{\cdot}68 - 315{\cdot}67\, m + 5{\cdot}810\, m^2$$
$$\text{P′ series } \nu = 17207{\cdot}44 - 308{\cdot}947\, m + 5{\cdot}528\, m^2$$
$$\text{Q series } \nu = 17206{\cdot}28 - \quad 6{\cdot}8052\, m^2$$
$$\text{R series } \nu = 16963{\cdot}57 - 342{\cdot}170\, m + 7{\cdot}0825\, m^2.$$

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